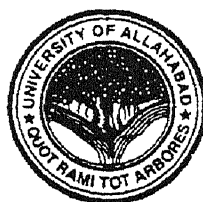


ION EXCHANGE SORPTION STUDY OF
SOME METAL IONS AND ORGANIC LIGANDS
IN SOLUTION



A

Thesis

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DOCTOR OF PHILOSOPHY

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Kirti Khare

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Department of Chemistry
University of Allahabad
ALLAHABAD

Kirti Khare
18-12-02
(Kirti Khare)

Glossary of symbols and abbreviations

$[]$	Molar Concentration
M	Metal
L	Ligand
ML_n	complex
N,n	Maximum number and number of ligands associated with metal in a complex
Σ	Summation of all the terms substituting all values of n
D	Distribution Coefficient
β_n	Overall stability constant
D_o	Distribution coefficient of metal ion in absence of ligand
I	Ionic strength
L%	Percentage loading
NH_4OAc	Ammonium acetate
OxAc	Oxalic acid
AcOH	Acetic acid
OX	Oxalate
Cit	Citrate
$(NH_4)_3Cit(OH)$	Triammonium salt of citric acid
λ	Distribution coefficient of complex
λ_1	Distribution of $[ML]$ species
λ_2	Distribution of $[ML]_2$ species
λ_3	Distribution of $[ML]_3$ species
K_1	Formation constant for 1:1 Complex of $[ML]$
β_2	Formation constant for 1:2 Complex of $[ML]_2$
β_3	Formation constant for 1:3 Complex of $[ML]_3$
K	Ion Exchange equilibrium formation constant

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CHAPTER – 1

INTRODUCTION

BRIEF PRESENT DAY ACCOUNT.

The scientific and industrial developments throughout the world and in our country have taken a standard growth of suitable level. But now most of the countries have achieved this level or goal, while others are following them. Overall results of these advancements are now showing the depleting effects on the nature and the living world including the human society. The poor and adverse effects are presently rising fast and may be seen as negative points in all areas and fields of country. We are also suffering from all these short-comings, imbalances and bad effects, therefore, all the sections of the society and masses have started showing concerned for this deep rooted conspiracy unknowingly flourished by us causing all sorts of troubles to people, animal and plant kingdoms. The developed townships, cities and urban areas are the major victims because of these factors along with migration and high concentration of men power due to job or other opportunities and the uncontrolled population growth. All these activities are leading to variety of pollution. A number of agencies and organizations, generating awareness about these pollution and associated problems, have started working to stop them and to work for minimizing them, if it is not possible to cut them completely.

Ion exchange is one of the simple and fundamental techniques applied for removing hardness of water, the phenomenon is a landmark discovery for welfare of the society. This technique is being vastly used for a large number of processings, involving the testing, detection, analyzing, separating, estimating and so many such type of treatments can be successfully and easily carried out by it.

HISTORICAL DEVELOPMENT

Ion exchange is a natural phenomenon, and in nature it is observed in inanimate soils, sands and rocks as well as living organisms. One of the note worthy exception in ion exchange is a solid interacts with solution (42). Thomson (64) an agriculture chemist, discovered the base exchange property of soils, and a similar observation based on the soil interaction with an ammonium salt and subsequently release of Ca^{2+} ions equivalent to NH_4^+ ions had been reported by Way, Lemberg and Weigner (77,78,48) had identified a number of natural materials possessing

properties, viz. clays, gluconites, zeolite and humic acid etc., Lemberg had also obtained amalcite ($\text{Na}_2\text{O}, \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) by leaching the mineral leucite ($\text{K}_2\text{O}, \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) with a solution of sodium chloride, and had found that transformation could be inverted by treating amalcite with a solution of KCl showing reversibility of the exchange process.

In the beginning of the twentieth century Harm and Rumpler (44) prepared first synthetic industrial inorganic ion exchanger, and Gans (54,55) attempted to utilize ion exchange process for industrial purpose, using synthetic aluminum silicates for softening water, and also for treating sugar solutions. An understanding and clarity of the concept of ion exchange phenomenon were worked out by the study of the crystal structures of these materials reported by Pauling (123). The historical significance and the developments of ion exchange phenomenon were compiled and presented by Duel and Hostettler (63). Among the excellent books on the subject are those by Nachod (43,45) Osborn (49), Kumin (153) and Samulson (144). A series of volumes on the advances in ion exchange has been edited by Marinsky and Marcus (79) in which a chapter of special interest in vol.5 in an "Ion exchange in elemental Analysis " by Strelow. A theoretical treatment of ion exchange phenomenon has been lucidly presented by Helfferich (42) Marcus and Kertes (193) and others (39,193,156), Giddings et. al. (81) in their books presented the recent advances in chromatography, and while the concepts and contrasts in chromatography has been vividly presented by Miller (82). Extensive listing of commercial ion exchangers and their properties have been prepared and presented by Dorfner (114). Applications of ion exchange phenomenon in analytical chemistry were discussed in detail and reported by Inezedy (83) Rieman and Walton (190) and others (113,82,83,120,52,1,65) while inorganic analyses in aqueous-organic solvent mixtures have been described by Korkish (86). Whereas Egoror and Makarova (40), and Sachse (50) have given a concise account of applications using ion exchange in radiochemistry.

The reviews on ion exchange chromatography by Chernobrov (159), Kuchne (51), Salmon (8082), Nozak (131), Petermann (67), and Das (68) describe the ion exchange technology in the purification of individual rare earths, the virtual

separation of lanthanides etc. The separation of platinum metals has been described by several workers and reported the results in their reviews (88).

The organic exchangers or resins are also composed of a skeleton and ionogenic or functional ion exchangeable groups like inorganic exchanging materials.

ION EXCHANGE RESINS

The skeleton of modern synthetic organic ion-exchangers is predominately formed by a copolymer of styrene with divinyl benzene (DVB). This elastic three-dimensional hydrocarbon network can be easily prepared and possesses sufficient physical and chemical stability suitable for various working conditions. The required ionogenic exchangeable groups can be attached to this skeleton by appropriate chemical reaction. The properties of such skeletons or resin frameworks are described by the ratio of the amounts of individual monomers used during their synthesis (29). Resins containing low DVB swell more in aqueous solutions. Large ions can easily diffuse through the exchanger and the exchange kinetics or process is fast. Mechanical strength of the skeleton decreases with decreasing proportion of DVB. Resin with frameworks containing a higher proportion of DVB (>15%) swell in aqueous solution is very high. Considering the high crosslinking, the number of ionogenic groups which can be attached to the skeleton is lower and decreases with increasing percentage of DVB. At the same time, the rate of diffusion of the exchangeable ions through the skeleton decreases together with a sieve effect from the skeleton three-dimensional networking. The skeleton can be composed of a mutually penetrating network formed by the individual chains. The sieve size is considerably heterogeneous and the structure of the skeleton formed is composed of low porosity. The pore size is given by the distance between the individual polymeric chains and is very low; the porosity appears only after the swelling of the resin. This type of exchanger is called microreticular resin. A skeleton of sufficiently large pores distributed throughout the whole skeleton volume is usually produced by additional cross-linking or by the modification of the porous structure (99) in the styrene-DVB matrix. It is usually called an isoporous framework but the most

common and relatively modern resins have macroreticular or macroporous structures (112). The size of the porous formed can be controlled during the skeleton preparation. They are much more resistant osmotic shock, have relatively a smaller swelling difference in polar or nonpolar solvent. The change of volume of the resin during its drying is also relatively small. This framework type resins are also possess a higher oxidation resistance (139,200).

The polymeric network skeleton or matrix can work as an ion exchanger only after having an ionogenic group onto the appropriate site of the skeleton matrix. A variety of resins with varying structures are now available possessing different skeletons or matrix with attached ionogenic groups (74,87) and thus according to the character of ionogenic groups the ion exchange resins can be characterized in the following classes:-

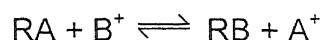
- I. Cation exchange resins (2,9,30,75,142,172,185) with an acid ionogenic or functional $-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{PO}(\text{OH})_3$ etc. groups.
- II. Anion exchanger (resin) (10, 37) with a basic ionogenic or functional $-\text{NR}_3\text{OH}$, $-\text{NH}_2$, $=\text{NH}$ and $\equiv\text{N}$ etc. groups.
- III. Mixed bed of cation and anion exchangers containing acidic and basic ionogenic groups and it used for removing the charged species completely.
- IV. Electron exchangers redoxites, available to perform redox reaction with a-NR_3^+ group.
- V. Selective ion exchangers (171) having specific ionogenic groups $-\text{N} \begin{smallmatrix} \text{CH}_2\text{COOH} \\ \text{CH}_2 \end{smallmatrix}$ interacting only with one type a group of ions and in an ideal case preferably selective to one type of ion only.
- VI. Exchanger of special properties have certain special behaviors, viz., decolorising, etc., which occurred due to its ionogenic groups, polarising effect induced to the contacting molecule causing its sorption on the exchanger.

Resins containing only one-type ionogenic exchangeable groups are called monofunctional or homoionic exchangers. Resins containing more than one type of ionogenic exchangeable groups ($-\text{SO}_3\text{H}$ and $-\text{OH}$; $-\text{COOH}$ and $-\text{SO}_3$ etc.) are called polyfunctional exchangers. However, monofunctional types of resins are

always preferred in analytical chemistry especially in separation procedure. Each ionogenic group has two portions, the one, which is fixed firmly to the resin skeleton by a covalent bond and a number of such bonds form a type of macro ion, known as the fixed ion. The other portion constitutes the ions of opposite charge, which are bound to the macro ion by electrostatic or ionic forces, and they are called 'counter ions'. These counter ions are also a part of the ion exchangers and can be exchanged for an equivalent amount of various ions (of the same type of charge) from the solution. Together with the counter ions oppositely charged ions (as compared with counter ions) diffuse from the solution into the interior of the resin during the ions exchange process. Denoting the resin skeleton as ' $-R$ ' and the attached ionogenic groups as ' $-SO_3H$ ', the ion exchanger can be written symbolically as ' $R-SO_3H$ '. According to the dissociation ability a various ionogenic groups of ion – exchangers in the form of free acids or bases, the ion exchangers can be classified as strongly, medium or weakly acidic (or basic). Resins with the acidic ionogenic groups, i.e., in the H^+ ions. Simultaneously the resin with basic ionogenic groups, i.e., in the OH^- form release OH^- ions. These processes can be expressed quantitatively by means of the apparent dissociation constants of the appropriate cation or anion exchangers. The round up pK values ($-\log K$) for different ionogenic groups of ion- exchangers are 1 ($-SO_3H$), 4-5 ($-COOH$), 9-10 ($-OH/phenolic$), 1 ($-NR_3OH$), 3-5 ($-NHR$, $-NR_2$) and 6-9 ($-NH_2$). The amount of exchange able ionogenic groups is fixed for an exchanger but varies to exchanger to exchanger. It is expressed quantitatively and the term is called exchange capacity of the resin. It is closely related to the composition of the resin skeleton as well as with the resin bead or particle size of the exchanger.

AFFINITY AND SELECTIVITY OF ION EXCHANGER

If the ion exchanger is added to an aqueous solution (free from complex forming substances) of an electrolyte, an exchange reaction between the ion exchanger and the ions in the solution takes place provided that the counter ion of the resin is not identical with the ions from the dissolved electrolyte. The exchange reaction of ions of the same charge takes place as.



If this reaction is carried out in closed system, reaction goes to equilibrium due to the fact that the ion exchange is a reversible process. Equilibrium concentrations of ions taking part in the exchange are not identical under equilibrium conditions. They are dependent on the value of relative affinity of the reacting ions to the ion exchanger as well as on their initial concentration. It has been experimentally ascertained, that the affinity (or in exchange potential) of various ions to the same resins in dilute solutions (<0.1M) increases with the ionic charge of ion investigated. Polyvalent ions are, therefore, attached to the exchanger more firmly under the same conditions as compared with the monovalent ions.

For ions of the same charge, it has been found that affinities are inversely proportional to the radius of the hydrated ions. More detailed comparative investigation have shown that affinity of cation to a series of ion exchanger similar or identical to the so-called lyotropic series. The affinity of anion is governed by similar rules. Moreover it increases with increasing polarisability of anions. The general trends follow to a affinity series of various ions but the order of affinities in the individual series varies slightly depending upon the individual nature of the exchanger and the conditions.

The difference in affinity between the individual ions is the key factor related to selectivity of the exchanger. The selectivity depends on the type and concentration of the interacting ions their inherent behaviour, and the natures of the solvent (medium) and exchanger. In principle, the selectivity of an ion exchanger depends on the following factors. For synthetic ion exchange resins:

1. Selectivity increases with increasing the content of DVB (i.e., divinyl benzene cross – linking percentage).
2. Ions with a smaller effective hydrated ionic radius are preferentially sorbed or taken up.
3. If the ionogenic groups of the resin form an ionic pair with the interacting ions, the resin selectivity of this ion is enhanced.

4. If substances present in the solution formed are undissociated compounds then those ions forming less undissociated compounds are taken up or preferred by the resin.
5. Resin selectivity is suppressed with the increase of temperature. It is a consequence of the rising in temperature resulting reduction in the ionic hydration shells (leading to a diminishing of the difference between the effective hydrated ionic radii of the reacting ions).

SELECTION OF SUITABLE ION EXCHANGER (137)

The analytical problem actually decides the choice of an ion exchanger having suitable inorganic groups, the ionic form, the skeleton its cross – linking (DVB%) and the porosity, the resin grain size and uniformity of the particle. Other factors like monofunctionality of the resin, its purity, mechanical, chemical, thermal or radiation stability etc, are also important to be taken into account. The degree of crosslinking of the resin affects the degree of swelling, the selectivity and the rate of equilibration resulting to change in the sorption or exchange of the species involved. Therefore a resin of low degree of cross linking swells of a high degree in leading to a considerable change in aqueous or solution phase volume, which changes the composition of the external solution. Naturally such resins are less suitable because the sharp differences in the affinities of the various ions towards the exchanger diminishes resulting to narrowing of the diffuse zone distribution in the column separation process of ions. The resins with a high degree of cross- linking are therefore, more preferable for such investigations needing less swelling but of high selectivity. They may have relatively low exchange capacity and poor ionic diffusion inside the resin bed, which leads in slow exchange kinetics. Also large ions can not penetrate into such resins due to the dense network of cross - bonds. Sometimes such resins may be used indirectly in ion exclusion chromatographic technique. Usually therefore a medium or average category cross-linking resins with about 8% DVB are commonly used. The choice of resin particles or grain size (mesh number) is important and is linked with the nature of the problem. The low or high grain sizes resins are

selected as and when required as per experimental necessity. Even exchangers with very fine particles or beds are used to have compact columns for special purposes.

Certain specific chemical problems can not be worked out on using organic resins, and these may suitably be resolved by using inorganic or liquid ion exchanger. (8,12,18,59,70,71,72,76,98,125,162,163,171)

Characteristics of Common Strongly Acidic Cation Exchanger (137, 10): -

1. Two types of exchanger phenolic polycondensates and styrene-DVB resins containing the $-\text{SO}_3\text{H}$ groups are mostly used and commercially available
2. Styrene – DVB resins are monofunctional.
3. The $-\text{SO}_3\text{H}$ ionogenic group is bound either directly to the benzene core or through methylene bridge.
4. Such exchangers (in H^+ form or any other form) take part in the exchange process almost 100% but the role of pH of the solution must be considered.
5. The degree of ionisation of the ionogenic groups corresponds to that of strong mineral acids (in case of H^+ form). The $-\text{SO}_3\text{H}$ group dissociates more easily as compared with the $-\text{CH}_2\text{SO}_3\text{H}$ grouping (long chain).
6. Chemical reactions of the H^+ form resin are comparable to that of sulfuric acid in solution.
7. The pH of the solution does not affect the exchange capacity of the resin appreciably, but it is ionogenic group of the resin which actually pH sensitive and accordingly affects the capacity. These resins can be used in all media (acidic, neutral or alkaline).
8. Selectivity of the $-\text{SO}_3\text{H}$ group increases with atomic number, valency and degree of ionisation of the exchanged element. Selectivity decreases with increasing ionic radius of the hydrated ion. But these are valid only appropriate dilute solutions or media. The sorption of monovalent ions in concentrated solutions is higher as compared with polyvalent ions.
9. A large excess of a strong acid of relatively high concentration is necessary to regenerate the resins completely into the H^+ form again and again.

10. Exchanger (styrene – DVB types) exhibits sufficient resistance towards oxidising agents, and solution of acids and hydroxides.

Characteristics of Common Medium Acidic Cation Exchangers (137, 10): -

1. Ion exchanger containing the $-\text{PO}(\text{OH})_2$ or $-\text{OPO}(\text{OH})_2$ groups of medium acidic dissociations are commercially available and used for the work particularly linked with related problems.
2. The chemical properties of these resins are comparable to those observed for phosphorous or phosphoric acids in solution.
3. The dissociation ability of the H^+ – form is between that of strongly and weakly basic cation exchanger, i.e., of average or medium of two.
4. The exchange capacity of these resins depends on the pH of the external solution. The effective pH value range, $\text{pH} > 5$, is found suitable for most of the mono– and divalent cation.
5. Naturally selectivity of the ionogenic groups of such resins depends strongly on the type of the sorbed ion and on the pH of the solution.
6. Only a small excess of a strong mineral acid as compared with the stoichiometry is necessary to convert the resin (already in the monovalent ionic form) completely into the H^+ – form. A considerable larger excess of an acid is needed in the case of other ions. If acid elution process fails to regenerate may required, the resin in the H^+ – form a suitable complex forming agent may required.

Characteristics of Common Weakly Acidic Cation Exchangers (137, 10):

1. The commercially available such resins are either monofunctional exchangers ($-\text{COOH}$ groups) prepared by copolymerization of acrylic or metacrylic acids with DVB or phenolic poly condensates of resorcylic acid ($-\text{COOH}$ and $-\text{OH}$ groups).
2. Resins in the H^+ – form can only be converted to salt – form at higher pH ranges as at lower pH dissociate of H^+ is difficult.
3. The degree of ionization of these resins corresponds to that of acetic acid in solution.

4. Their exchange capacity depends strongly on the pH value of the external solution. The effective pH range is 6 -14.
5. High selectivity of H^+ ions is a characteristic property of them. The selectivity series of alkali metal ions was found to follow the reverse order as compared with that for strongly acidic cation exchangers. The resins also exhibit a relatively high affinity for the alkaline earth metal ions.
6. A small excess of a strong mineral acid as compared to stoichiometry is sufficient to convert the resin into the H^+ – form.
7. These resins can also be utilized for the isolation of single and complex organic bases.
8. The resins can be used as a buffer in operations where a low activity of the H^+ ion is necessary.
9. On converting these resins (H^+ – form) in other ionic forms, great volume changes occur.

Characteristics of Common Strongly Basic Anion Exchangers (10, 13, 22, 41, 88, 97, 124, 129, 134, 140, 162, 187, 193, 196)

1. Commercially available such type of resins are styrene- DVB copolymers, and differ according to functional groups present, methylinium, – $N^+(CH_3)_3Cl^-$ (Type I) and pyridinium – $N^+(CH_3)_2C_2H_2OHCl^-$ (Type II).
2. Resins having –OH exchangeable functional groups when interact with salts solution corresponding base is formed and the resin is converted to the corresponding salt - form.
3. Usually the degree of ionization of ionogenic groups of these resins corresponds to that of the alkali metal hydroxides. Resins in the OH^- – form sorb even very weakly dissociated acids (boric, silicic). The basicity of resins Type I is higher than that of Type II.
4. Their exchange capacity does not depend appreciable on the pH of the solution.
5. Selectivity of such resin towards anions increases with increasing valency of the ion and decreases with increasing hydrated ionic radius.
7. A large excess of sodium hydroxide solution (~ 2% NaOH) is needed to convert the resin completely into the OH^- – form especially when the resin is in the Cl^- –

form. Regeneration or conversion of type II is relatively fast than type I. These anions exchangers operate in the whole pH range (preferably 1-13). They can be used in highly concentrated acids (e.g. 12 M HCl) and are sufficiently resistant towards strong solutions of acids and hydroxides as well as, towards certain oxidizing agents. Type I is more resistant as compared with type II, especially in the OH^- – form.

Characteristics of Common Medium Basic Anion Exchangers (137, 10): -

1. The exchange behaviours of these resins lie between those of the strongly and weakly basic ion exchangers. The resins contain strongly as well as weakly basic ionogenic groups (predominantly tertiary amine groups – $\text{N}^+\equiv$).
2. If their ionogenic groups have been regenerated with sodium hydroxide solution, the resins will separate neutral salts. If the resins have been regenerated with solutions of sodium carbonate or ammonium hydroxide they behave as weakly basic resins.

Characteristics of Common Weakly Basic Anion Exchangers: (137, 10): -

1. Commercial products used such resins based on styrene – DVB polyamine epichlorhydrine or phenol – formaldehyde carrier skeletons.
2. Resins contain ionogenic groups $-\text{NH}_2$ (or substituted amines) $-\text{NHR}$, and $-\text{NR}_1\text{R}_2$ (Primary or secondary amines).
3. They are not able to separate neutral salts with the formation of the corresponding acids.
4. The degree of ionization of the ionogenic groups is analogous to that of ammonia.
5. Resins in the form of free base, sorb strong mineral acids with the formation of the appropriate salts. Acidic forms of the resins liberate acids when in contact with water due to hydrolysis.
6. The exchange capacity of these resins depends strongly on the pH of the solution and on the valency of the sorbed ion.

7. A series of this type of resin is able to bind some substance by vander Waals forces. The amine groups of these resins are able to form strong complexes with various ions (Ag^+ , Cu^{2+} etc.).
8. Regeneration of the resin to a free base can be carried out with only a small stoichiometric excess of sodium carbonate, sodium hydroxide or ammonia (or even aromatic amines),
9. The resins are sufficiently stable only in dilute solutions of acids and hydroxides.

TECHNIQUE AND METHODOLOGY OF ION EXCHANGER

Separations of various metal ions or charged species are achieved by 'batchwise operation', and/or 'column operation' methods.

Batchwise Operation (5): - Batch operations are involving the equilibration technique where in the conditioned cation or anion exchanger (resin) is equilibrated with the suitable fixed solution phase containing the species to be separated the attainment of equilibrium is facilitated by appropriate stirring or mechanical shaking. A number of trial experiments should be performed to work out the equilibration duration for the particular experiments. After the completion of equilibration period the two phases (solid resin and aqueous solution phases) are separated by more filtration, decantation, centrifugation etc. The concentration of the concerned species are now estimated both in the exchanger and solution phases, and on the basis of amounts practically found out are used for calculating the distribution coefficient of the species in a suitable range of interacting or reacting complexing ligand. The separation possibilities are evaluated from these measured distribution coefficient values. The amount of exchanger or resin and the concentration of separating species in the solution are also decided by the trial experiments, but they should be always finalized with respect to the capacity of the exchanger or resin, the selectivity criteria of the resin and the possible practical affinity of the species with respect to composition of the solution, and the requirements linked with the determination method applied for that species. Batch operation data give a practical and possible information regarding the possibility of the separation but final practical

separation could be worked out by utilizing batch information to column chromatographic or dynamic equilibrium process, which gives the real profile of the separation scheme.

Batch equilibration data can also be used for the determination of structural aspects based on evaluation of charges present on exchanging species, and for evaluating the stability parameters of simple and complex species, as well as evaluating the selectivity coefficient etc. The technique is simple and it also gives information for the systems, which could not be, worked out by application of ion-exchange technique, therefore, ruling out or vestige of time by investigating further those systems. Therefore the batch process is widely used for collecting the equilibration data to be utilized for column operations and subsequently achieving the perfect or ideal separation.

2. Columnar operations: (61,150): - These are most widely adopted methods because ion exchange processes are equilibrium reactions necessitating a continuous contacting of the exchanger with fresh electrolyte solution or eluting agent in order to drive the reaction to completion. The columnar operation is essentially an elaborate multiple batchwise technique in which the uppermost portion of the column is constantly contacting fresh electrolyte solution eluting agent whereas the lower portions are being contact with electrolyte solution or eluting agent which is sorbed by the upper portion of exchanger and may be of low concentration. This procedure leads the exchanger bed to become fully exhausted at the top first and then gradually downwards.

On the basis of experience by the trial experiments a general columnar procedure is developed, which is usually used with, desired slight deviations or modifications according to requirements of the particular separations. It involves selective sorption, washing with proper medium solution (mostly aqueous or water miscible organic solvents), and regeneration (elution of retained or loaded ions) (94) which may sometimes clubbed with the second step.

Selective sorption (15, 103) is based on a choice of suitable sorption conditions for one species or the element or for a small group of species or elements present in the mixture to be separated. The sorption conditions are

selected, and so adjusted that the species of interest may be performed or retained move in the exchanger and the other species or component should accordingly not to be taken up due to decrease in its sorption. The complexation is one of such frequently used processes and has diverse impacts on the sorption tendencies by enhancing the difference of the selectivity factors. Selectivity of sorption can also be affected, by the characteristics of exchangers, i.e., strongly acidic/basic, cation and anion exchangers in an appropriate ionic-form. The selection of species or elements by the exchanger is selectivity dependent on the pH of the solution, and on the stability constant of the concern complex.

The selectivity elution process may be considered as the reversal of selective sorption. Again it is the chemistry of the species involved which governs the elution in a manner that one type of the retained ions is desorbed from the ion exchanger under the adjusted conditions unaffected other ions which remains firmly bound on the exchanger (and do not move down along the exchanger bed). When short columns are used then separation process is accelerated and it takes less time. While long columns take more time but the separations are sharp. Separation processes using the method of selective elution are mostly based on the difference in stability constants of various complex species of elements to be separated.

Simple chromatographic elution procedures are found unsuitable or most of the time not applicable to be applied successfully for achieved the separations of complicated metal ion mixture. Accordingly procedures of maximum efficiency should be worked out and trailed to have desired goal. Three types of chromatographic column operations, i.e., frontal, displacement, and elution analysis are commonly used depending on the nature of separations of species. Displacement and frontal analysis are of limited importance in the separation of inorganic ionic mixture at least quantitative separations of individual components could not be achieved. Elution chromatography is one of the most widely used processes for the separation of such inorganic ion mixtures. It also ensures quantitative separation of the individual components and with high resolution and efficiency. The disadvantage of this operation is that only a small amount of solute can be analyzed. If larger amounts of the substances are separated, complications

may arise during the elution due to cross-contamination between the individual separated components. Therefore, a proper modification is desired to be applied to the assembly which can be improved and method can be extended to mixture having larger quantities of components, and process may be found of commercial utility. Materials in the form of ion exchange papers are in use of certain purpose. They can be prepared by a dispersion of very fine resin particles in paper pulp or by a direct synthesis of an inorganic ion exchanging material in a paper band. The practical technique for applying these materials is similar to that of paper chromatography. Ion exchanging materials can also be used in the form of thin plates or various type of membrane. The practical procedure corresponds to the technique used in thin layer chromatography or the electrochemical technique using membranes as separating media.

The principle of elution chromatography depends on the fact that the analyzed mixture of ions is sorbed on the top of the resin bed as a thin band. The separation is carried out with a suitable eluting solution, which is poured to the column from the top. During the downward movement of the elution solution, the composition of the sorbed species is continuously changing and ions of lower affinity move faster down the column, while ions of relatively higher affinity (to the exchanger) move more slowly. After a sufficient amount of the eluting solution has been passed down the column, the individual component of the separated mixture is distributed along the ion exchanger column in the form of separated sharp bands. In an ideal case, they flow out separately one by one from the column in the eluting solution. There is always a certain volume of the eluting solution, which contains the binary mixture of two adjacent components.

However even the most practical eluting process may suffer some complications, due to the non-ideality of the system and broadening of the individual bands (zone) as a consequence to the difference of the concentration gradient within each component species band. Tailing may occur due to sluggish desorption by the eluting agent and such problems may be solved only by entirely different approach or treatment using the chemistry aspects instead of physical parameters of chromatography.

Formally, the batchwise operation was considered to be of little importance, but later its utility was realized and shown in practice by many workers. Modern studies of ion exchange are none generally based on the use of the batch analysis technique, as the results obtained are in a more systematic pattern and the theoretical predictions for separations are easily possible. The theories of batch and column separations are closely related to each other. If a separation by batch operation is nearly possible, a simple column operation can often be used with a short column, a minimum of elution and washing will only be necessary. Therefore, it is preferable to obtain perfect separation conditioned by batch operation, and then actual separation is achieved by the column technique. If however, the difference in the exchange distribution coefficients of two ionic components is very small, the batch technique will not provide a satisfactory separation. In such cases a column has to be used, and several columnar trial experiments will provide the exact procedure to be applied for separating the species.

APPLICATIONS (153)

A large number of ion exchange resins with various functional groups and different properties are now days commercially available and are used in research laboratory to industrial plants (8, 100). Major applications of analytical requirements like isolation and concentration of trace elements removal of interfering components, deionisation, determination of total salt content, purification and preparation of various chemicals or solutions, in qualitative and quantitative determination, etc. (41). These all are basically requirements involving the separation and which is solved by the use of ion exchange principle and methodology, and successfully the separation of mixture solutions of rare earths, actinides Zr-Hf, Nb-Ta, Mo-W etc. have already been developed and achieved by this simple technique.

The manifold application of the ion exchange resins is pre concentration and isolation of trace charged species (like recovery of radium from seawater). (62, 128, 152, 167, 3, 55, 56). Water softening and electrodialysis, (54, 131, 24, 26, 31), water analysis (57, 89, 104, 100, 101, 108, 109, 113, 133, 135, 145, 168, 170, 182,

192, 28, 90), analysis of rocks, materities and lunar samples (88, 110, 102, 111, 136, 138, 143-154, 160 -184, 195, 4, 21, 20). Analysis of fission products, nuclear rare materials and the separation of isotopes and rare earth elements (32, 33, 53, 73, 88, 91, 107, 108, 118, 194, 7, 19, 22, 26, 27, 35, 47, 69, 88, 96, 134, 143, 149, 177, 178, 179, 180, 181, 180, 186, 188, 192, 189, 11, 16, 17), application of biological samples (70, 92, 125, 130, 36, 139, 151, 196, 46, 58, 60, 93, 94, 95), resin spot test (118, 119, 163, 199, 24,), purification of sugars (25), catalysis and pharmaceuticals. (25, 131), special uses like ion selective electrodes (66, 198), ion exchange membranes and ion exchange fibers (71, 124), Hydrometallurgy (131).

This chapter – 1 presents a brief account of the introduction describing the scope and use of ion exchange technique and ion exchange materials especially ion exchange resins.

The theoretical aspects and the different quantities related with the ion exchange equilibrium studies are given in chapter– 2.

In chapter-3 have devoted for general ion exchange equilibration study in binary mixed mixture media of NH_4OAc - OXAc (at constant AcOH). The exchanger used was cation exchange resin, Amberlite IR-120, in NH_4^+ – form and anion exchange resin Amberlite IRA – 400 in Cl^- – form. Distribution coefficient values calculated from experimental data and stability constant or formation constants values were evaluated using Schubert's approach for cation exchange study and Froneaous approach for anion exchange study.

Similar types of investigations were performed for ammonium citrate media in chapter – 4.

The metal – EDTA complex distribution study in resin and solution phase described in Chapter – 5. In these investigation used same anion exchange resin Amberlite IRA – 400 in Cl^- – form. The number of various distribution coefficients

and ion exchange equilibrium constants were evaluated using the experimental parameters.

The general discussion work and a summary of main finding are given in Chapter – 6.

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CHAPTER – 2

QUANTITIES AND THEORIES OF ION EXCHANGE EQUILIBRIUM

Ion exchange phenomenon may be considered either as reaction obeying the law of mass action (11) or as Donnan equilibrium between the inside liquid of the resin particles and the outside solution (12,23). Donnan theory adequately explains the volume changes (swelling) on replacing one ionic species by another (23). An equilibrium is reached between the osmotic pressure of the hydrated ion and the backpressure of the 'elastic' framework of the crosslinked polymer. The amount of crosslinking influences the 'elasticity' of exchanger (resin) and hence the equilibrium between the ions. The concentration gradient is an important parameter governing the distribution of the ion involved. The amount of distributing ionic species therefore inside the resin matrix with the concentration of that ionic species in the solution (57).

In equilibrium when an ion exchanger is placed in an electrolyte solution containing a counter ion, which is different from that in the ion exchanger, both ion exchanger and the solution contain competing counter ion species. The various quantities used for describing ion exchange equilibrium are (33):

- i) **Ion Exchange Isotherm (31,37):** - It is the graphical representation which shows the ionic composition of the ion exchanger as a function of the experimental conditions. The equivalent ionic fraction of the counter ion 'M' in the ion exchanger is plotted as a function of the equivalent ionic fraction in the solution, keeping other variable constant. In a system in which the ion exchanger shows no preference for M or M', the equivalent ionic fractions in the ion exchanger are the same as those in the solution resulting in a linear and diagonal isotherm. Actual ion exchangers in general, select one counter ion in preference to the other, and thus selectivity of the ion exchanger requires a deviation from the linear and diagonal isotherm, i.e. a non-linear isotherm would result.
- ii) **Separation Factor (31, 57, 55):** - The preference of the ion exchanger for one of the two counter ions is often expressed by the separation factor (α). It is the quotient of the concentration ratios of the two counter ions in the ion exchanger and the solution, thus

$$\alpha_{M'}^M = \frac{\bar{C}_M \cdot C_{M'}}{\bar{C}_{M'} \cdot C_M}$$

where,

$\alpha_{M'}^M$ = Separation factor for counter ionic species M and M'

\bar{C}_M and $\bar{C}_{M'}$ = concentration of counter ions M and M' in the Exchanger (resin) phase.

C_M and $C_{M'}$ = concentration of counter ions M and M' in the Solution phase.

It is dimensionless factor but depends on the total concentration of the solution, the temperature, and the equivalent fraction i.e. equivalent ion fraction expressed ion molalities/molarities. It is applicable for the calculations of the column performance, especially when synthetic resin beads are being used as an exchanger for column operation.

The interstitial volume of absolute interstitial volume or 'Void' volume of the ion exchanger column is the space between the swollen resin particles i.e. the volume occupied by the mobile phase in the packed section of a column. This 'Void' volume (V_i) can be defined as the total bed volume (V_t) reduced by the volume of the swollen resin. This quantity V_i should be predetermined for calculating retention data or explaining experimental results obtained by performing column chromatography. A variety of methods have been developed for the determination of V_i , which also take into account the type and the crosslinking of the resin employed. Generally the V_i values of resins of higher cross linking ($\geq 8\%$ DVB) can be determined using water soluble substances with sufficiently large molecules like polyvinyl, polystyrene, sulphonic acid etc., which are not able to penetrate into the resin phase due to their greater molar volume or high charge. But the V_i values of resins of low crosslinking because of their adsorbing capacity for simple small ions due to Donnan equilibrium can be determined by passing the solution containing the same ions as the ionic form of the resin of the column. Another quantity called relative interstitial volume or interstitial fraction is often used in addition to V_i

and it is expressed as,

$$\text{Relative Interstitial Volume, } v_i = \frac{V_i}{V_t}$$

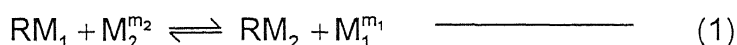
The value of relative interstitial fraction are linked with the shape & the size of the resin grains /beads as well as on the state of the resin bed in the column (57)

- iii) **Selectivity coefficient (34,58):-** The equilibrium is usually established such that the amounts of both ions in the equilibrium solution or on the resin are not equal.. The resin exhibits some degree of preference for one ion relative to the other (even when they are present in equivalent quantities)

This is the phenomenon of selectivity or relative resin affinity for competing ions in ion exchange process. This property is expressed quantitatively in terms of various selectivity coefficients and constants.

A number of different approaches have been made to predict selectivity of various resins for different ions. A rigorous thermodynamic treatment is of limited practical use (due to the fact that numerous exact measurements are needed before the distribution can be calculated). It is probably easier to measure the selectivity (Selectivity coefficient) directly using a formal thermodynamic mass action expression e.g.

where,



m_1, m_2 = absolute charges of the ions M_1 and M_2 respectively.

R = exchanger (resin)

$m_1 = m_2$ for equation (1)

for this reaction the true thermodynamic equilibrium constant K_a is represented by the expression

$$K_a = \frac{a_{RM_2} \cdot a_{M_1}^{m_1}}{a_{M_2}^{m_2} \cdot a_{RM_1}} \quad \text{—————} \quad (2)$$

where, 'a' is the thermodynamic activity of the components. In order to calculate K_a , it is necessary to ascertain the activities of the individual

components in both phases. However, it is very difficult to obtain experimentally the a_{RM} and a_{RM_2} values equation (2) can be transformed into the form

$$K_a = \frac{[RM_2]^{\gamma_{RM_2}} \cdot [M_1]^{\gamma_{M_1}}}{[M_2]^{\gamma_{M_2}} \cdot [RM_1]^{\gamma_{RM_1}}} \quad (3)$$

where, $[]$ represents the analytical concentrations of the individual components. The symbol ' γ ' represents an activity coefficient. Applying the law of mass action for Equation (1) the quantity or the relativity coefficient ($k_{M_1M_2}$) is giving

$$k_{M_1M_2} = \frac{[RM_2][M_1]}{[M_2][RM_1]} \quad (4)$$

The true thermodynamic constant K_a can be expressed by the equation

$$K_a = k_{M_1M_2} \cdot \frac{\gamma_{RM_2} \cdot \gamma_{M_1}}{\gamma_{M_2} \cdot \gamma_{RM_1}} \quad (5)$$

Selectivity coefficient are also called the concentration constant or distribution quotient is the measure of the measure of the relative affinities of various ions for a particular ion exchanger.

The selectivity coefficient is not a constant. Its value depends on-line ionic size and the total ion concentration the solution. It is also affected by the chemical structure of the resin and, to some extent, by its exchange capacity.

- iv) **Distribution coefficient:** - In certain practical application, equilibrium is most conveniently expressed in terms of the distribution coefficients, D , of the counter ions. The distribution coefficient of a solute is defined as the ratio of the concentrations of the solute in the ion exchanger and in the solution. Distribution coefficients are also expressed in terms of molalities and molarities.

Generally the selectivity of a separation is expressed by the ratio of distribution coefficients of competing species, M and M' , i.e.,

Selectivity coefficient \neq Separation Factor ($\propto \frac{M^{p+}}{M^{q+}}$)

or ,

$$\alpha_{M'}^M = \frac{D_M}{D_{M'}}$$

where the mass distribution coefficient is given for ionic species, M by

$$D_M = \frac{\text{Amount of M on resin}}{\text{Amount of M in solution}} \times \frac{\text{mL Solution}}{\text{g dry resin}}$$

Similarly, a volume distribution coefficient can be defined by replacing 'gram dry resin by Volume wet resin.

The position of the elution peak of ionic species, M in a chromatographic elution process is given by simple expression,

$$\overline{V}_M = [D_M \times m + \text{dead space (mL) of the column}]$$

where , \overline{V}_M is the elution volume of M in mL , D_M is the mass distribution coefficient and m is the mass of dry resin (in g.) on the column , (17,86) , This equation is the guide for the analytical chemist intending to employ ion exchange chromatography for quantitative analytical separations

A number of modified equations, predicting not only the position but also the shape of the elution peaks and the amount of cross contamination, are also available (16, 25). In case of asymmetrical elution curves the information obtained by the application of above-mentioned equation is incomplete due to the inhomogeneity of resin crosslinking or other factors. To take these factors into account one has to rely on empirical information. Experiments of a column loaded to 1% of its total capacity the deviations from such prediction are negligible. But for higher loads the appearance of the first traces and the position of the peak maximum require lower elution volumes with increasing loads, and can be approximately estimated (56).

Two basic requirements have to be met to obtain favorable conditions for a good separation, i.e., the separation factor and kinetics of the separation. The preference of ion exchanger for one of the two counter ions is often

expressed by the separation factor (α). This quantity is important in practice for the calculation of column performance. It is quotient of the concentration ratios of the two counter ions in the ion exchanger and the solution or the ratio of the distribution coefficient (D).

$$\text{Separation factor, } \alpha_{M'}^M = \frac{[M]_r \cdot [M']_{aq}}{[M']_r \cdot [M]_{aq}} = \frac{D_M}{D_{M'}}$$

where ,

$[M]_r$, $[M']_r$, $[M]_{aq}$ and $[M']_{aq}$ are the molar concentrations of M and M' in resin (r) and aqueous (aq) phases. If the ion M is preferentially associated the factor $\alpha_{M'}^M$ is larger than unity, and if M' is preferred the factor is smaller than unity. As separation factor (α) is the ratio of the equilibrium distribution coefficients of the separating species M and M' the distribution coefficient (D) of the more strongly sorbed species M must be high enough for its quantitative retention, and that of the less strongly sorbed species (M') must be low enough for reasonably fast elution.

The kinetics of the separation is governed by the physical exchange process of the species to be separated, but this exchange interaction is also linked with the chemical reaction going on in the solution phase, as well as the affinity considerations of the species towards the exchanger. It is again associated with the accommodating space available in the exchanger for the incoming species and its affinity as well as the hydration volume of the exchanging species. These factors together controlled the resulted kinetics of the separation process. Therefore, for separations carried out by column operations must be followed by favourable kinetics (78, 90,). For common practical purposes, the only important merit is that the separations are worked out by comparing the distribution coefficient values (D) followed by the separation factor (α) values which give the idea of possibility for a practical feasible separation for a binary system, i.e., involving two species. Yet during an actual experiment of binary separation with a calculated separation factor value of ten times more may prove to be much fruitful, than another with a

factor of thousand times more, because in the later case it shows bad tailing of the less strongly retained species.

The increased selectivity in ion exchange separations are achieved by the choice of proper exchanger and this has been carried out by attaching ion selective groups such as phosphonic (10), phosphoric (10,39,56), dipicrylamine (77), phenylfluorene (79), diphenylcarbazi- -de(80), dimethylglyoxime (41) , chromotropic acid (41), resorcinol (58), hydroquinone (57), pyrogallol (58), hydrosulphide (65) and thiol groups (26) or chelate forming groups such as anthranilic acid (27) , salicylic acid (20): 8-hydroxyquinoline (21),glyoxal-bis-2-hydroxamine (9), phenylthiourea (28) orthohydroxybenzenearsonic acid (84) , amino acids (27) and amino polyacetic acids (15,6,29,75,88) to polystyrene and other salts of resin matrix. Furthermore, various selective inorganic ion exchange materials, such as insoluble phosphates (2,3,35,42,43,82), molybdates (38,72,74), tungstates (44,73,75), arsenates (24), antimonates (4,7,67), selenites (62) , and silicates (83) , have been used ; and also the oxides of Fe(III) (48), Sn (IV) (21), Mn(II') (59), Ti (IV) (50), Al(III) (76), Si (II')(4) ,Th (IV) (68) and Zn(II) (5) ; and many complex cyanides (8,30,40,60) have been investigated for their selective character.

Separation factors for cation exchange chromatography of alkaline earth elements in aqueous hydrochloric or other acids (not forming complexes with these elements) are rather small (85,86,87) .A number of complexing media having such as acetate (22,31), format (84) citrate (61), lactate (53) malonate (79), α -hydroxy isobutyrate (70,89), EDTA (13) ,DcyTA (72,87) , EGTA(72), 2,6-pyridinedicarboxylate (13) and acetylacetonate (27), have therefore been tried to enhance separation of these elements. In almost all cases these were used and a systematic procedure was developed empirically by testing a few eluting agents in a suitable concentration range and selecting the best one. A comparative study of distribution coefficients, from which the most favourable and possibly feasible among the various investigated eluting agents, provides the information of evaluating the merits of these reagents.

A separation factor (α) value of ~ 10 is worked out on trial basis and is found in most of the cases the good separation can be achieved in that particular medium for the adjacent pairs of binary systems.

Two very important requirements of an exchanger are insolubility and chemical stability, some times the temperature also plays effective role and become important (47, 1, 14, 49). The insolubility is closely related to its swelling tendency. The higher the percentage of crosslinking in the framework of an exchanger, the lower is the flexibility and so it's swelling. Despite the strong swelling the chemical stability remains satisfactory, Swelling and sorption equilibria have received particular attention with organic ion exchange resins, where these phenomena were initially noted, and are more pronounced. Ion exchangers both organic and inorganic, sorb or take solvents from the solution phase and expand or 'swell' so the exchanger's matrix which is considered like a framework of elastic springs, is stretched and exerts a pressure or 'swelling pressure' on the internal pore liquid resulting in the increase of exchanger's volume. Ion exchangers swell only to a limited degree, after which equilibrium is attained many resins are sufficiently porous to permit ready access of solvents and ions without under going a great deal of swelling. Generally they swell in order to accommodate very large ions. In general, the results show that the more polar solvents cause greater swelling than the non-polar hydrocarbons and the more porous resins swell more than their less porous analogues. In mixed solvents, many of resins examined showed greater swelling than in either of the solvent alone depending on the dielectric constant of mixed solutions. The swelling properties of cation exchange resins have been investigated by Grrissback (25) and in detail by Samulson (79) and Gregar et al (27). Changes in swelling cause movements of the filter, which is commonly known as the 'filter breaths' it may cause stoppages or the formation of channels in the exchange column. The more open the framework of the exchanger, the greater is the swelling and more pronounced the breathing of the filter with a rather dense framework is, therefor, preferable (78). The extent of swelling is favoured by (33).

(i) Polar solvents,

- (ii) Low degree of cross-linkage of the resin,
- (iii) High capacity of the resin,
- (iv) Strong solvation tendency of the fixed ionic groups present in the resin.
- (v) Large and strongly solvated counter ion,
- (vi) Low anionic charge of the counter ion.
- (vii) Complete dissociation of the counter ion in the resin, and
- (viii) Low concentration of the external solution.

ION EXCHANGE CAPACITY

It is necessary to determine the number of active exchangeable groups capable of taking part into the exchange process. The ion exchange capacity is the total number of such groups per unit weight of the exchanger or resin. Its measurement is commonly referred to as the cation or anion exchange capacity for cation or anion exchanger, respectively. Ion exchangers are characterized quantitatively by their capacities, i.e., the equivalents of number of counter ion present in a specified amount of exchanger. Apart from this simple definition which is sufficient and practicable, other definitions or quantities have also been proposed and used to reflect the effect of the operating conditions. A most accepted definition is the number of inorganic groups present in the specified amount of ion exchanger i.e., the amount of exchanger which weighs one gram when it is completely converted to hydrogen (H^+) or chloride (Cl^-) form and is devoid of sorbed solutes and solvents. It is also expressed either as scientific weight capacity (meq/g dry hydrogen or chloride form of exchanger) or as technical volume capacity (meq/L packed exchanger bed) in hydrogen or chloride (or OH^-) form for the fully water swollen exchanger. The capacity for the cation exchange resin in milliequivalent per gram (meq/g) is usually calculated by the expression (87).

$$\text{Cation exchange capacity} = \left(\frac{a \cdot b}{w} \right)$$

Where,

‘a’ is the normality of [NaOH] solution,

‘b’ is the volume in mL of NaOH used.

‘w’ is the weight of the resin in g.

similarly, the capacity of an anion exchange resin is given are milliequivalent per gram (meq/g) (V_2) is calculated by the expression.

$$\text{Anion exchange capacity} = \left(\frac{b.v}{w} \right)$$

Where,

'b' is the normality of $[\text{AgNO}_3]$,

'v' is the volume of AgNO_3 used, and

'w' is the weight of the resin in g.

Theoretically all the sites of a resin must be occupied by ions but it may be more or less completely loaded with some particular ion. Some other terms or quantities are also used for describing the capacity of an exchanger (33) :

(a) Apparent Capacity: - It is the equivalent number of exchange cable counter ions per specified amount of the exchanger. It is lower than maximum real capacity when ionic groups are incompletely ionized or not taking part in the exchange process. It depends on the P^{H} and the concentration of the solution etc.

(b) Sorption Capacity: - The amount of the counter ion as the neutral solute when taken up by the absorption or adsorption instead by ion exchange processes for a specified amount of the exchanger is known as the sorption capacity of the exchanger. It depends on experimental conditions and the nature of the exchanger.

(c) Useful Capacity: - Another term is used for the capacity when equilibrium is not attained and there it depends on ion exchange rate and related parameters.

(d) Breakthrough or Dynamic Capacity: - The capacity which is utilized until breakthrough of the sorbed species occurs, and is used in column operations and depends on the experimental operating conditions.

(e) Base Capacity: - This term is given for mineral exchangers. It depends on the grinding of the exchanger, and expressed on a ionic function of the degree of grinding (38)

ION EXCHANGE LOADING

It is an important practical parameter directly linked with the ion exchange capacity, and may be considered a is its exponent. Loading of a sorbable species may be defined as the ratio of the amount (in mg) of the ionic species taken up (per

gram of exchanger or resin) to the initial amount present in the solution. The loading (L) may be expressed as :-

$$\text{Loading (L)} = \frac{\text{mg of soluble ionic species taken up/g or g exchanger or resin}}{\text{mg of that ion initially present in the solution}}$$

It is dimension less quantity but depends on the characteristics of the exchanger or the resin as well as on the total concentration of the ionic species initially selected. The percentage-loading (L%) gives the idea of the percentage of metal ions transferred to the exchanger or resin phase when it is shaken with solution containing the ionic species.

The loading (L) of a cation exchange resin by a cationic species (M^{n+}) is defined by the relationship.

$$L = \frac{n[M^{n+}]}{C}$$

where,

'n' is the charge of the metal ion, M^{n+}

' $[M^{n+}]_r$ ' is the concentration of M^{n+} in the resin phase and 'C' is the capacity of the resin.

The percentage of loading is evaluated by the relationship,

$$L\% = \left[\frac{D}{v + D} \right] \times 100$$

where,

'D' is distribution coefficient and

'v' is the total volume of the aqueous phase (mL).

The loading measurements are also essential to be evaluated for a number of systems. Since the selectivity coefficients are varied with the fraction of exchangeable sites occupied by the ions, the measurements are performed at various loading volumes, and the selectivity coefficients are normalized at a certain loading value by interpolation or extrapolation (85)

All above described quantities/factors or the parameters are practically determined data and are used to investigate the nature of chemical reactions. The species present in the system, and the mechanism of exchange processes of

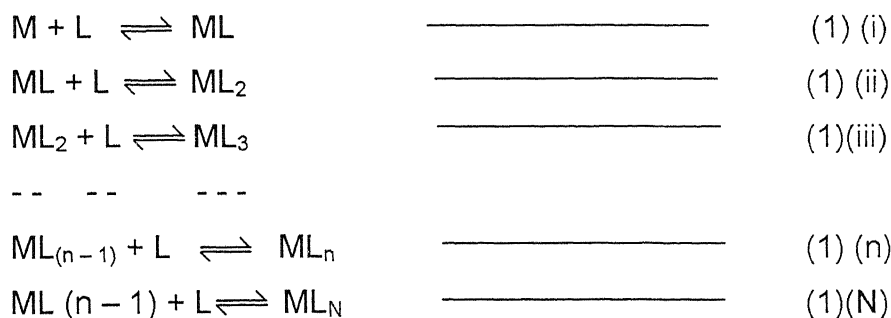
respective particular species as well as the behavior and nature of the exchanger used.

STEPWISE METAL - LIGAND EQUILIBRIA

After the enunciation the love of mass action in 1864. Studies on chemical equilibrium were under taken by measurements based on solubility, partition, electrical conductance, potential etc. But these techniques had successfully been applied to limited system mainly because there was a lock of theoretical back ground in the understanding of solution equilibria. Later developments were made in the context of never concepts which there light on the effects of other phenomenon existing simultaneously in equilibrium systems and the most practical and informative parameters. The equilibrium constant especially in metal, complex systems were for the first time determined by potentiometric and/or solubility measurements and also by partition experiments.

The occurrence of intermediate steps in equilibrium systems were for the first time proposed by N. J. Bjerrum and later his son, J. Bjerrum gave in detail the investigation of stepwise equilibrium constants in metal-ligand systems. This had to a new direction of studies in metal complex in solution and attracted worldwide attention. Schwarzenbach (82) and their associates soon reported excellent work in this field.

The formation of a metal complex in solution at a given temperature occurring in steps may be represented by a series of equations of the type.



The charges on the metal ion M and the ligand L, being omitted for convenience. The step formation constants K are given according to Bjerrum (B₂) by following equation.

$$K_n = \frac{[ML_n]}{[ML_{(n-1)}][L]} \quad \text{-----} \quad (2)$$

where,

n may have values 1, 2, 3,.....N, here K_n is called nth metal ligand stability constant. As a first approximation [] represented the concentration instead of activities.

The overall stability constant or gross constant β_n is the product of $k_1, k_2, k_3 \dots \dots k_n$ and is defined as

$$\beta_n = \frac{[ML_n]}{[M].[L]^n} = \sum_{(n-1)}^n k_n \quad \text{-----} \quad (3)$$

In all the equilibria described above the metal ion is written without specifying charge or degree of solvation but are important to be taken into consideration for the discussion of complexation or chelate effect, etc (18).

With only a few exceptions, there is generally a gradually descending progression in the values of the stepwise formation constants in a metal-ligand system. Typically as ligand is added to the solution of metal ion the formation of first complex species, ML, is initiated immediately and also very fast the other higher species till the free metal ion concentration reduced to an equilibrium concentration. Further addition of ligand is being continued, the formation of ML_2 species enhances rapidly, and the ML concentration starts dropping and subsequently. The next higher species, ML_3 becomes dominant. ML and ML_2 becoming unimportant, and so forth, until the highest complex ML_N is formed, bearing the system with very-very reduced equilibrium concentration of lower species at very high ligand concentrations.

There are several reasons for a decrease in stepwise formation or stability constant values for a metal-ligand system as a number of associated ligand increase:

- (i) Statistical factors.
- (ii) Increased steric hindrance as the number of ligands increase, if ligand molecules are bulkier than the water molecules, they replace.
- (iii) Columbic factors effective mainly in complexes with charged ligands (63) or with polar ligands.

The statistical factors may be treated in the systems where the coordination number remains the same throughout the series $[M(H_2O)_n] \dots [M(H_2O)_{(N-n)} L_n] \dots [ML_N]$. The $[M(H_2O)_{(N-n)} L_n]$ species has n sites from which to lose a ligand, whereas the species $[M(H_2O)_{(N-n+1)} L_{(n-1)}]$ has $(N-n+1)$ sites at which to gain a ligand. Thus the relative probability of passing from $[M(H_2O)_{(N-n+1)} L_{(n-1)}]$ to $[M(H_2O)_{(N-n)} L_n]$ is proportional to $(N-n+1)/n$. Similarly, the relative probability of passing from $[M(H_2O)_{(N-n)} L_n]$ to $[M(H_2O)_{(N-n-1)} L_{(n+1)}]$ is proportional to $n/(N-n+1)$. Hence on the basis of those statistical considerations above,

$$\frac{k_{(n+1)}}{K_n} = \frac{\left[\frac{(N-n)}{(n+1)} \right]}{\left[\frac{(N-n+1)}{n} \right]} = \left[\frac{n(N-n)}{(n+1)(N-n+1)} \right]$$

In a number of cases on comparing the experimental ratios of successive formation constants and those calculated from the above expression, it is found that the experimental ratios are consistently smaller than the statistically expected ones, which is typical and shows that the other factors are also important.

There are cases where the experimental ratios of the formation constants do not remain constant even having changed monotonically same because one of them is singularly large and other is small. The associated and responsible factors are:

- (i) An abrupt change in coordination number and hybridization at some stage of the sequence of complexes.
- (ii) Special steric effects that become operative only at a certain stage of coordination, and
- (iii) An abrupt change in electronic structures of the metal ion at a certain stage of complexation.

When an exchanger is in equilibrium with a metal complex solution, there are three equilibria coexisting in the system:

- (i) Metal complex equilibrium in the aqueous phase.
- (ii) Metal complex equilibrium in the resin phase, and,

- (iii) Partition equilibrium of the sorbing species between aqueous and resin phases. The existing cationic or anionic species would distribute depending on cation or anion exchanger used.

In the resin phase, if it is assumed that the complex forming equilibria occur in a similar way as in the aqueous phase, then for the resin phase, the step formation constant and overall stability constant can be described in case of solution equilibria and may be expressed in the same way.

$$K_n = \frac{[ML_n]}{[ML_{(n-1)}] \cdot [L]} \quad \text{_____} \quad (4)$$

$$\beta_n = [M] \cdot [L]^n = n_{(n-1)}^n \cdot k_n \quad \text{_____} \quad (5)$$

Partition or distribution constants related to various species (coefficients of ligand Metal and cationic species) can be given by a series of expressions:

$$\lambda_L = \frac{[L]}{L} \quad \text{_____} \quad 6(L)$$

$$\lambda_o = \frac{[M]}{M} = Do \quad \text{_____} \quad 6(M)$$

$$\lambda_1 = \frac{[ML]}{ML} \quad \text{_____} \quad 6(I)$$

$$\lambda_2 = \frac{[ML_2]}{ML} \quad \text{_____} \quad 6(II)$$

$$\lambda_{(n-1)} = \frac{[ML_{(n-1)}]}{ML_{(n-1)}} \quad \text{_____} \quad 6(n-1)$$

$$\lambda_n = \frac{[ML_n]}{ML_n} \quad \text{_____} \quad 6(n)$$

where, λ_2 , λ_o and λ_n are distribution coefficient of ligand, metal and of nth cationic complex, respectively from equations (3), (5) and (6)

$$\overline{\beta}_n = \frac{\lambda_n \beta_n}{\lambda_o \lambda_L^n} \quad \text{_____} \quad (7)$$

$$\overline{\beta_n} \lambda_L^n = \frac{\lambda_n \beta_n}{\lambda_o} = \lambda_n \quad \text{—————} \quad (8)$$

The distribution of total metal concentration between resin and aqueous phases can be give as :

$$D = \frac{[M] + [ML] + [ML_2] + \dots + [ML_{n-1}]}{[M] + [ML] + [ML_2] + \dots + [ML_n]} \quad \text{—————} \quad 9(i)$$

By converting metal concentration of resin phase in terms of aqueous phase using equation (6)

$$D = \frac{\lambda_o[M] + \lambda_1[ML] + \lambda_2[ML_2] + \dots + \lambda_{n-1}[ML_{n-1}]}{[M] + [ML] + [ML_2] + \dots + [ML_{n-1}]} \quad \text{—————} \quad 9(ii)$$

and rearranging by applying equation (3),

$$D = \frac{\lambda_o[M] + \lambda_1\beta_1[M][L] + \lambda_2\beta_2[M][L]^2 + \dots + \lambda_{(n-1)}\beta_{(n-1)}[M][L]^{n-1}}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \dots + \beta_n[M][L]^n} \quad \text{—————} \quad 9(iii)$$

$$D = \lambda_o \frac{1 + \frac{\lambda_1\beta_1}{\lambda_o}[L] + \frac{\lambda_2\beta_2}{\lambda_o}[L]^2 + \dots + \frac{\lambda_{(n-1)}\beta_{(n-1)}}{\lambda_o}[L]^{n-1}}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n} \quad \text{—————} \quad 9(iv)$$

Now, from equation (8)

$$D = \lambda_o \frac{1 + \lambda_1[L] + \lambda_2[L]^2 + \dots + \frac{\lambda_{(n-1)}}{\lambda_o}[L]^{n-1}}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n} \quad \text{—————} \quad 9(v)$$

$$D = \lambda_o \frac{1 + \sum_{n=1}^{n=n-1} \lambda_n[L]^n}{1 + \sum_{n=1}^n \lambda_n[L]^n} \quad \text{—————} \quad 9(vi)$$

$$\frac{D}{\lambda_o} = \frac{\left(1 + \sum_{n=1}^{n=n-1} \lambda_n[L]^n\right)}{F} \quad \text{—————} \quad 9(vii)$$

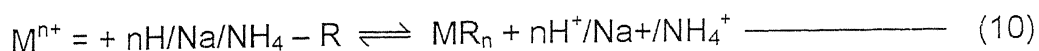
where,

$$1 + \sum_{n=1}^n \beta_n \text{ is denoted } F$$

METHOD OF SCHUBERT

The investigation of complexation equilibria solution by ion exchange technique has been found more important and valuable, when the system involves complex species of dominating ionic nature. It has specific quantitative indirect considerations. When the exchanger phase acts as a separate solid medium. Though the factors like inhomogeneity of the exchanger phase due to variation in its grain size, the distribution of exchanging sites, the adsorption of the solvent or the solution containing the dissolved species by the exchanger, the swelling or the shrinkage of the exchanger matrix and the related hydrolytic pressure affect the equilibrium drastically, therefore, the ion exchange equilibrium may not be exactly found practically equivalent to normal solution equilibria. The results obtained based on practical observation determined by this technique are always differing to certain degree because of these above-mentioned factors. Even then the ion exchange results are important because these are fulfilling the practical needs more correctly and an useful manner by the industries and the pilot plant etc.

For the systematic approach correlating solution equilibrium theories applying with desired modification and approximations carries out the ion exchange treatment. Systems containing both a single complex and several complex species can be evaluated by the relationship, which exists between the amount of metal sorbed on the ion exchanger (resin) and the concentration of free metal ion in the solution. If only a single neutral or negatively charged complex is present in the systems the use of a cation exchanger eliminates the possible sorption of any species other than the metal ion. In such a case the amount of metal sorbed on the cation exchanger is directly proportional to the concentration of free metal ion in the solution. The amounts of cation exchanger, the ionic strength, the pH and the temperature must be maintained constant during taken experimental observations. The general equilibrium between the ion exchanger (resin) and the metal ion is,



Since very low concentration of metal ion is taken, no appreciable change in the H^+ or Na^+ or NH_4^+ concentration occurs in either phase. Then the ion exchange equilibrium for the reaction (equation –10) is

$$K_{ex} = \frac{([MR_n][Na^+ / H^+ / NH_4^+]^n)}{([M^{n+}][H / Na / NH_4 - R]^n)} \quad (11)$$

In presence of ligand [L], the metal ion complexation is expressed as,



And the formation constant (k) is given as

$$k = \frac{[ML_n]}{[M^{n+}][L^{-}]^n} \quad (13)$$

The distribution coefficient of the metal ion between the aqueous solution and the exchanger (resin) is,

$$D = \frac{[MR_n]}{[M^{n+}] + [ML_n]} \quad (14)$$

when no ligand is present in the solution, the metal ion distribution coefficient is designated as D_o , and which equals to,

$$D_o = \frac{[MR_n]}{[M^{n+}]} \quad (15)$$

Because distribution $\left[(H^+ / Na^+ / NH_4^+)^n / (H / Na / NH_4)^n \right]$ either of H^+ or Na^+ or NH_4^+ remains constant.

Thus the metal ion concentration in solution,

$$[M^{n+}] = \frac{[MR_n]}{D_o} \quad 16(i)$$

on substituting in equation (38) gives

$$[ML_n] = \left[MR_n \left(\frac{1}{D} - \frac{1}{D_o} \right) \right] \quad 16(ii)$$

On substituting the value of $[M_n^{+}]$ and $[ML_n]$ into the equation (37) of formation constant (k) then.

$$K = \frac{[(D_o - D) - 1]}{[L]^n} \quad (17)$$

The ligand concentration $[L]$ is known initially taken for each experiment, and D_o and D values are determined by measuring the equilibrium metal ion concentrations in the solution and the exchanger phase after the experiment. Both k and n (the number ligand molecules associated with the metal ion) can be evaluated by graphical method, i.e. by using the logarithmic form of the above equation.

$$\log \left[\left(\frac{D_o}{D} \right) - 1 \right] = n \log [L^{-}] + \log k \quad (18) (i)$$

Alternatively, the equation may be rearranged to have,

$$D^{-1} = D_o^{-1} + [L^{-}]^n \cdot k \cdot D_o^{-1} \quad (18) (ii)$$

and a plot of D^{-1} Vs $[L^{-}]^n$, for the proper n value, will be linear in nature (a straight line) which extrapolates to D_o^{-1} when $[L] = 0$. Schubert () used his method originally for single complex species systems. His method was further modified also to deal with the stepwise formation of a series of complex species. The modified version of the method is none most often applied with some specific features. A suitable ionic medium should always be used to provide constant cation concentration, but it is assumed that the variations of the ligand concentrations have no effective change in activity coefficients appreciably. A constant pH (When the ligand is an ion of a weak acid) and a low metal ion concentration are used so that the effective ligand concentration is proportional to ligand concentration initially taken. Complexation is assumed producing only natural or anionic species and which are not to be taken by the exchanger (resin). This assumption is a distinguishing feature of Schubert's method. It is further assumed that if cationic complex species are produced, the cationic exchanger (resin) must not take them. The Schubert's modified approach and its most commonly used form is,

$$\frac{[(D_o / D) - 1]}{[L]} = \beta_1 + \beta_2 [L] + \dots + \beta_n [L]^{n-1} \quad (19)$$

This may be solved for the various formation constants (β_n) by successive extrapolations the method is best applicable to the chelating ligand-systems because of the formation of possibly only the natural or anionic complex species, Also in such cases the number of associated ligand molecules would be possible low, i.e. 1 or 2, and then the association or formation constant of such systems is obtained directly from a simple linear form of the above equation (19)

COMPUTATION OF STABILITY CONSTANTS BY METHOD OF FRONAEUS

Fronaeus procedure makes use of the function

$$F_1' = \left[\frac{(\lambda_o / D) - 1}{[L]} \right] \quad (20)$$

which can be calculated from measurements of λ_o , D and [L]. Therefore, a system in which cationic complex species ≤ 2 , a combination of equations (8), (9). And (10) gives.

$$F_1' = \frac{\beta_1 - \lambda_1' + (F_2 - \lambda_2')[L]}{1 + \lambda_1'[L] + \lambda_2'[L]^2} \quad (21)$$

where function F2 is derived from the following equation

$$F = 1 + \sum_1^n \beta_n [L]^n \quad (22)(i)$$

$$F = 1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 + \beta_4 [L]^4 + \dots \dots \dots \beta_n [L]^n \quad (22)(ii)$$

$$F_1 = (F - 1) / [L] = \beta_1 + \beta_2 [L] + \beta_3 [L]^2 + \beta_4 [L]^3 + \dots \dots \dots + \beta_n [L]^{n-1} \quad (22)(iii)$$

$$F_2 = (F_1 - \beta_1) / [L] = \beta_2 + \beta_3 [L] + \beta_4 [L]^2 + \dots \dots \dots + \beta_n [L]^{n-3} \quad (22)(iv)$$

$$F_3 = (F_2 - \beta_2) / [L] = \beta_3 + \beta_4 [L] + \dots \dots \dots + \beta_n [L]^{n-3} \quad (22)(v)$$

$$F_3 = [(F_1 - \beta_1) / [L]] - \beta_2 / [L] = \beta_3 + \beta_4 [L] + \dots \dots \dots + \beta_n [L]^{n-3} \quad (22)(vi)$$

$$F_3 = (F_1 - \beta_1 - \beta_2 [L]) / [L]^2 = \beta_3 + \beta_4 [L] + \dots \dots \dots + \beta_n [L]^{n-3} \quad (22)(vii)$$

or, in general,

$$(F_1 - \sum_1^{t-1} \beta_n [L]^{n-1}) / [L]^{t-1} = \beta_t + \beta_{t+1} [L] + \dots \dots \dots + \sum_{t+2}^n \beta_n [L]^{n-t} \quad (22)(viii)$$

Extrapolation of the plot F_1' against [L] to zero free ligand concentration gives.

$$F_{10}' = \lim_{C_L \rightarrow 0} = \beta_1 \lambda_1' \quad (23)$$

The resultant value of $(\beta_1 - \lambda_1')$ is used to calculate another function.

$$F_2 = \frac{(\lambda_0/D)[(\beta_1 - F_1)[L] - 1] + 1}{[L]^2} \quad (24)$$

equation (10) and (11) also gives

$$F_2' = \frac{\beta_1(\beta_1 - \lambda_1') - \beta_2 + \lambda_2[(\beta_1 - \lambda_1')(F_2 - F_3)][L]}{1 + \lambda_1' + \lambda_2'[L]^2} \quad (25)$$

where,

$$F_{20}' = \lim_{[L] \rightarrow 0} F_2' = \beta_1(\beta_1 - \lambda_1') - (\beta_2 - \lambda_2') \quad (26)$$

From equations (10), (11) and (14)

$$F_2' = \beta_1 F_1' - F_2 + \lambda_2'(F_1'[L] + 1) \quad (27)$$

where,

$$\frac{(F_2' - F_{20}')}{[L]} = \frac{\beta_1(F_1' - F_{10}')}{[L]} + (\lambda_2' - F_1' - F_3') \quad (28)$$

At low free ligand concentrations, the plot of $(F_2' - F_{20}')/[L]$ against $(F_2' - F_{10}')/[L]$ will, therefore, be a straight line of slope β_1 . Once β_1 and k_1

is known, the term $(F_2' - F_3')$ can be calculated from equation (16). Combination of equations (10) and (17) gives a quantity.

$$v = F_2' - \beta_1 F_1' + \lambda_0(\beta_2 - \lambda_2')D.[L] \quad (29)$$

$$v = \beta_2 F_1' - F_3 \quad (30)$$

The value v may be calculate from equation (19) and that of β_2 may be obtained from the limiting slope,

$$\lim_{F=0_1} dv/dF_1' + \beta_2$$

of the plot of v against F_1' . Substitution of β_2 into equation (20) gives the power series F_3 , and since corresponding values of $[L]$ have been measured, the stability constants β_3, \dots, β_n may be calculated from the plot of function F_3 against $[L]$ using equation (12).

If M, metal and ML, first complex species are the only cations present, i.e., cationic complex species = 1, and $\lambda_2 = 0$, in the system, then equation (17), reduces to

$$F_2' = \beta_2 F_1' - F_2 \quad \text{—————} \quad (31)$$

Thus once the value of β_2 has been determined, the stability constants $\beta_2 \dots \beta_N$ may be calculated from equation (12). This simpler procedure may sometimes applied without serious error even for the systems in which cationic complex species = 2, if the value of λ_2 is much lower than λ_0 or λ_1 .

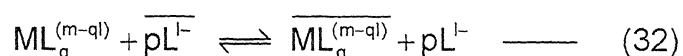
Graphical methods are based on the extrapolations permitting the determination of one parameter as the intercept and an approximation to another as the slope, or linear plots yielding two parameters as intercept and slope, while curve fitting allows the simultaneous determination of two parameters and an approximation of a third.

An elaborate and reigrous treatment for the computation of stability constant had been given by H. Loman and E. van Dalen (51), their method uses the a number of cation exchangers differing in their divinly benzene percentages or because of this difference in DVB% the preference of one species drastically affected in comparison to other. The method also utilizes this unique property for evaluating the metal-ligand equilibrium constant in solution phase. One has to use suitable numbers of different exchanger according to possible cationic complex species present in the investigating solutions. This method is relatively much more precise and accurate, and can successfully be used for determining the stability constant with the accuracy of equivalent to methods like potentiometry, polaragraphy or speetrophotometry etc. The only limitation of method is that further high degree of accuracy is achieved in system were the complex species present are passing the more electrovalent character, i.e., the inherent basic requirement of the ion exchange phenomenon. But the investigating system is pressing complex species are differing with respect to sorption tendencies more then this limitation will no more be effective practically, and result this obtained may be comparable to those of ionic type species.

MARCUS-CORYELL TREATMENT

The anion exchange study of metal ligand complexation equilibria involves a vary high electrolyte concentration leading to resin invasion, which is resulted due to use of high ligand concentration to have more formation of high degree anionic species. But for ideal equilibrium studies a dilute solution is desired, therefore, for anion exchange studies it may be considered an important limitations of the approach be cause the anion exchange treatments fail to take into account such considerable deviations of ligand activities from the ideality.

Marcus and Coryell have proposed practical and feasible treatment to overcome such experimental limitations of anion exchange approach for evaluating the equilibrium constant (54). Their rigorous treatment considers all the activity coefficients in terms of mean ionic activity coefficients ('a') of electrolytes. Anionic complexes can undergo exchange with the ligand inside the resin too.



'm' change of metal ion

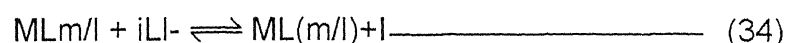
'l' change of anionic ligand

'q' anionic index (7 m/l)

'p' is the number of ligand molecules essential for electron equality, and the thermodynamic constant for this reaction is given as,

$$K_p^T = \frac{\overline{a_{MLn}} a_L}{a_{MLn} a_L^p} \quad (33)$$

Concentrations of complex species in the resin phase and as well as in the aqueous phase can be summed, and the ratio of the sums equal to molal distribution coefficient (D_m) for the metal, M. If only one complex species, i.e., the first anionic complex is found to be distributed between the two phases, then thermodynamically equivalent expressions are obtained for it. Where a metal complex species also exists simultaneously an alternative and applicable treatment is given taking into account the natural complex species concentration instead the free $[M^{n+}]$.



Coefficient i may be both positive and negative. The thermodynamic constant at equilibrium with the resin or exchanger phase can be expressed by usual simple

relationship. Two assumptions are made for approximation and extrapolation of the stability constants:

(i) Constancy of overall formation constants or stability constants holds in the resin phase exactly as in case of aqueous solutions, and (ii) the use of ligand activity in the resin phase is approximated like in aqueous phase. The effective activity coefficient of the ligand irrespective of the presence of different cation holds similarly in the resin phase solution. It has been shown that Harned's Rule is obeyed by the resin solution, and in principle it is possible to calculate the mean activity value of the mixed system. The effective resin ligand activity (\bar{l}) is evaluated as,

$$\text{Log}[\bar{L}] = \text{Log}[L] + \frac{l}{C+l}(\log \bar{m}_L - \log \bar{m}_C + \log(l/d)) \quad \text{--- (35)}$$

' \bar{m}_L ' is the morality of ligand in resin phase.

' \bar{m}_C ' is the morality of cation in resin phase.

' l ' Change on ligand

' C ' change on cation

Since the ligand activity function $\log[L]$ is an experimentally determinable its derivative can be calculated or alternatively a corrected distribution function, can be used.

$$\log D_o = (\log D - p \log L) \quad \text{--- (36)}$$

The slope of the corrected distribution curve is, thus, equal to the overage change of the complexes present in the solution, (expressed in units of the ligand change, l). The treatment proposed by Fronaeus (23) is applicable to use the corrected distribution curve, rather than the curve optioned from experimental data to incorporate the resin invasion in the Marcus-Caryll's treatment (55).

KRAUS AND NELSON TREATMENT

Kraus and Nelson have worked out the anion exchange approach for evaluating the equilibrium constants of anionic species by applying a little different approach and had proposed the treatment of analyzing the anion exchange distribution curve involving metal-ligand complexation by taking into account the bulk electrolyte ratio equal to one is to one (1:1).

Assuming that the only higher anionic complex species is taken up by the exchanger, then the exchange equilibrium reaction (equation 23) is expressed as-

$$\frac{K_p^T}{G_p} = \frac{\overline{ML_q^{p-}} m_L^p}{(\overline{ML_q^{p-}}) m_L^p} = \frac{(\overline{ML_q^{p-}})}{\sum m_n} \times \frac{m_L^{[L]^{p-}}}{m_L^{-p} [L]^p} \quad (37)$$

$$= D_m \frac{1}{\alpha_q} \frac{m_L^{p-}}{m_L^{-p}}$$

or, the metal fraction as complex species in the aqueous phase

$$\alpha_q = D_m (G_p / K_p^T) \left(\frac{m_L}{m_L} \right)^p \quad (38)$$

where,

G_p is the appropriate of the ionic activity coefficients of the ions involved in the exchange. If $[L]$ and D_m are known as functions of the ligand concentration and if the charge 'p' of the resin complex is known, the values of $\left(\frac{G_p}{K_p^T} \right)$ as a function of $[L]$ can be estimated, and the fraction of the metal in the form of complex species ML_q^{p-} in the aqueous phase, α_q are the primary results of Kraus and Nelson's treatment and complex formation or stability constants can be evaluated from these α_q values by application of standard extrapolation methods.

At high ligand concentrations α_q approaches unity, and the parameter

$$\left(\frac{K_p^T}{G_p} \right) \text{ may be evaluated by plotting } D_m \left(\frac{[L]}{[L]} \right)^p \text{ vs } [L].$$

It is observed that the treatment of Kraus and Nelson differs from that of Marcus and Coryell, though the results by both the methods are comparable. Different assumptions are involved in the two methods and it is difficult to judge which more nearly represents the 'true' behavior. But is also important that in certain cases Marcus-Coryell approach works better than the Karus and Nelson treatment while for some other systems the later approach given more reliable and practical results.

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CHAPTER – 3

**CATION AND ANION EXCHANGE STUDY OF
METAL IONS IN MIXED NH_4OAc - OXAc MEDIA
AT CONSTANT AcOH**

The technique of ion exchange involves the two phase equilibrium studies (78) in which the solid phase is usually an ion exchanger and the liquid phase is either simple aqueous solution or the miscible aqueous-organic solvent medium (43, 83). The general experimental procedure follows the distribution of charged species or the anion/cation among these above mentioned two phase (37). It is kind of heterogeneous two phases equilibria, which is not, in principle, considering the uncharged species present in the system or in the solution phase (22).

A variety of systems had been carried out by application of this simple principle, and several landmark separations like of rare earths (17), actinides (49, 40), Zr-Hf(54), Mo – W (108, 112), precious metal (81, 51), etc. have successfully been achieved, and applied to a number of purposes related to various type of analysis (110, 63). Such specific and well-defined separations were achieved by performing a huge number of trial experiments using different type of media. Among the inorganic media the mineral acids were widely used and a good number of selective and specific separations have been worked out. Kraus et al for the first time present their pioneering work in a very systematic way on the anion exchange of metal chloride complexes (65, 66, 67) salt of these acids have also been suitably used and fruitful separation results were reported.

Apart simple acids or their salts, sequestering agents (10, 65, 95, 93, 77) have been found in certain cases more useful, and subsequently the interest has been diverted towards use of inorganic complexing media (60, 57, 58, 59) Further, concentration have been made to organic complexing/cheating agents (38, 22, 9, 43, 90, 38) because of their more useful and specific effect. However, thiocyanate which is a simple anion, provides significant inorganic complexing medium, therefore it has been investigated in detail (10, 6, 60, 57, 58, 59, 62, 63, 30, 31, 36, 44, 80, 85, 29, 23, 43).

Ion exchange column chromatography is found a more effective, powerful and practical method for the separation of closely associated charged species, and is applied in a number of ways to achieve the desired separation. It also eliminates the factors associated with adsorption and precipitation reaction usually encountered in batch solvent extraction procedures.

Ion exchange equilibrium studies and investigation in aqueous and aqueous organic miscible systems have established broad fundamental characteristic as well as many interesting details and application related to complexation behaviours of chemical species. Korkish and Coworkers (65, 63) are pioneer and they started an intensive program (65, 66, 67) of anion exchange investigations with complexing metal ions putting emphasis of involving water miscible organic solvents in order to facilitate the complexation to higher degree leading anionic complexes formation. Applications and behaviour of anion exchange from solutions containing water miscible organic solvents have been found more valuable than cation exchange results because in such media the complexation resulted to the formation of anionic species. Selective sorption of cations by such process of anionic species formation and the anion exchanger in the presence of suitable complexing eluants has solved many typical difficult separations, viz., actinides and lanthanides etc. Mixed solvent media based on water miscible organic solvents have been freely used (30, 67, 60) to probe such separations with much ease. Separation factors are affected by the difference in resin phase solvent and solution phase solvents compositions, i.e., the conditions which are leading to superposition of partition chromatography on the ion-exchange chromatography (10, 23, 51). Iguchi (51) found that anion exchange eluting agent increases sorbabilities of sulphites, sulphates and thiosulphate and they can be successfully separated from selenites and telluride.

Several studies have been reported to work out and assess the efficient of various resins. The temperature effect on uni-univalent NH_4^+/H^+ or Ti^+/H^+ and di-divalent $\text{Cu}^{2+}/\text{Zn}^{2+}$ or $\text{Cu}^{2+}/\text{Mg}^{2+}$ or uni-divalent, NH_4^+ , H^+ , $\text{Ti}^+/\text{Mg}^{2+}$, Cu^{2+} , Zn^{2+} and $\text{I}^-/\text{C}_2\text{O}_4^{2-}$ exchange systems with Amberlite IRA – 400 anion exchanger resin have been evaluated by Singare et al (93, 101, 78, 7).

Katzin and Gebert (54) have investigated for the first time the sorption of electrolytes on the resins from mixed-miscible organic solutions in presence of relatively excess ligand contents with those metals forming very stable anionic complexes. They have also taken into consideration the secondary cation effects (15, 46, 44). For non-aqueous or mixed media such association was found as an important factor in both the phases. Expert for some spectrophotometric data (86, 88) and some cases of loading beyond the capacity (104, 67) no convincing

evidence has been produced to give the information about the association and the actual predominating species. Treatment of trace metal distribution data between an anion exchange resin and non-aqueous or mixed solutions depends mainly on the ion-pairing tendency of the ions.

In this chapter the complexation reactions between some metal ion (Mg (II), Al(III), Mn(II), Fe(II), Fe(III), Ni(II), Zn(II)) with ammonium acetate-oxalic acid medium in presence of acetic acid (constant) have been investigated and the stepwise stability constant have been determined using anion exchange technique. Mahan and Dey (83), Sarjanini et al (95,96,97) and Ohzeki et al (84) applied and successfully evaluated the stability constant by ion exchange methods for metal dyes systems. The method is essentially those of Froneous (26), Marcus-coryll (76) and Kraus-Nelson (65) which involves the determination of the distribution coefficients of the metal ions and the cationic as well as anionic complex species under a variety of conditions. The metal ligand complexation behaviour has been investigated in a relatively high ion concentrations or ionic- strengths (I) but at low acidities and the experimental data were suitably treated to obtain the values of the stability constants. Behaviour of a number of elements in ammonium salts as malonate (98), format (103) citrate (82), lactate (74), and acetylacetone (13) have been related a comparative study of coefficients provides the most favourable eluent concentration range which can be determined directly and concluding the suitability evaluation and comparison of different eluting agents suggested by Strelow et al (99). They have also investigated a member of complexing/chelating agents to work as good eluting agents. Large number of metal ions were studied using acetate, formate, lactate, citrate, tartrate, meliate, malonate, acetylacetonate, α -hydroxyisobutyrate, EDTA, DeyTA, EGTA, NH_4Cl , HCl , HClO_4 , etc. with the resin AG 50w – x 8 a cation exchanger. For the separation of Be from Mg, ammonium malate (0.05, pH-7) has been found to be the best eluting agent, while, citrate, malonate, and tartarate media are also satisfactory (99,98) Ammonium acetylacetonate (pH-9) is effective for the separation of Ca-Mg, while ammonium malonate (pH-7) is also suitable. A mixture of Sr-Ca can be separated satisfactory by application of ammonium acetylacetonate (pH-9) (99) or ammonium citrate (pH—9) (99) or ammonium α -hydroxy isobutyrate (0.70M) (98). For the separation of larger amounts of Sr from a mixture containing

small amount of Ba, ammonium α -hydroxy isobutyrate (1.20M, pH-7) has been found to be the best complexing eluting agent (84, 99, 110) while 1.0M ammonium lactate (74, 99) or 0.43M ammonium malate (99) or 0.55 M ammonium malanate (99, 98) all at pH 7.0 are also found to be satisfactory for the separation of Sr-Ba studies on the nature of rare earth species bound to the resin and that present in the solution phase in ammonium- α -hydroxy isobutyrate and ammonium lactate media have been made. It was found that 1:1 lanthanide- α -hydroxy isobutyrate or lactate species predominate in the resin and 1:3 lanthanide- α -hydroxy isobutyrate or lactate species predominant in the solution phase, at higher concentrations of above salts under normal analytical conditions (7, 11,). Studies in $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{CO}_3$ media have also been reported. In $(\text{NH}_4)_2\text{SO}_4$ medium can be separated from Ce (III) and La (5), and Mg from Ca and Sr (64). In $(\text{NH}_4)_2\text{CO}_3$ medium. Extraction of Mo from seawater has also been reported (95).

The behaviour of a number of elements in acetate medium have been investigated by Wiesenberger (111), Samuelson (103) and Diurfelt (21) and several separations were suggested, but the results obtained were of little practical value. Minami and Ishimori (81) described the separation of Ba and Pb by aqueous ammonium acetate at pH 6.1 using R-NH₄ type resin, while Honda (48) reported the separation of Mg, Ca, Sr and Ba. Khopkar and De (19) studied the cation exchange behaviour of Ba on Dowex 50w-x8 and obtained a high value for the separation factor with respect to Pb. The separation of heavy metal ions; Ag, Pb and Hg (II) has been reported by De and Majumdar (21), De et al (20) also separated Mg from Ca in limestone from acetate medium. Word and Choppin (112) studied the nature of rare earth species present in solution and that bound to resin phase. At higher ammonium acetate concentration they reported that the principal predominant species in solution is $\text{Ln}(\text{OAc})_3$ and in resin phase is $\text{Ln}(\text{OAc})_2$ and suggested that separations are comparatively very-very poor than other complex media. By ion exchange method Tedesco et al (105) studied the Cr(III) acetate system and investigated the nature of Cr(III) species present both in resin and solution phases, while metal ion nitric acid ammonium acetate systems using cation and anion exchangers were investigated in detail by Day et al and Gupta et al have also reported the separation of Hg (II) from other cations (35,83).

Oxalic acid is a powerful complexing agent with two carboxylic acidic groups showing its dibasic characters with dissociation constants, $K_{a1} = 5.40 \times 10^{-2} \text{ mol}^{-1}$ and $K_{a2} = 5.2 \times 10^{-5} \text{ mol}^{-1}$ at 30°C (106). Because of the low value of the second dissociation constant. The species usually dominant in solution are $\text{H}_2\text{C}_2\text{O}_4$ and HC_2O_4^- (100). A mixed system study of picolinic acid-oxalic acid catechol metal ion ternary systems for Ni(II), Cu(II) and Zn(II) were reported by Chaturvedi et al (15a). The catalytic behaviour of oxalic acid in aqueous acetic acid medium was suitably used to study the kinetics of the oxidation of some aromatic azo compounds which appears due to the complexation activity of the oxalic acid with Cr species to be reduced resulting the oxidation of azo compound (102).

Farid Khan (25) was used polarographic technique to determine the value of solution stability of Cd- α -alaninate-oxalate system at pH 8.40 and at ionic strength 1.0M KNO_3 , he also studied the Cd-oxalate system and confirmed the formation of three complex species, viz., $[\text{Cd}(\text{OX})]$, $[\text{Cd}(\text{OX})_2]^{2-}$ and $[\text{Cd}(\text{OX})_3]^{4-}$ with over all stability constants $\log \beta_{01} = 2.00$, $\beta_{02} = 4.69$ and $\beta_{03} = 7.08$, respectively. Cu(II)-oxalate system has been investigated polarographically by G. S. Monku et al (36). A Mcauley et al (1) and by J. Stary et al (53) studies of Fe (III) have also been performed using polarographic method in presence of oxalate (107, 88) Mahmoud et al (M8k) determined the formation constant of Cu(II) and Fe(III) ternary complexes with pyruvate and oxalate using polarographic technique. Srivastava et al (101) investigated the stability of mixed ligand complexes of Fe(III), Co(II), Zn(II) and Cd(II) involving oxalic acid as a primary ligand and glutathione as the secondary ligand in aqueous solution (at ionic strength, $I = 1\text{M } \text{KNO}_3$) and at a constant temperature.

The efficiency of an ion exchange resin depends on its capability of exchange of one type of ion with another (53). Several studies have been reported to workout and assess the efficiency of various resins (72, 73, 4).

The proposed study includes the distribution coefficients determination of a number of metal ions: Mg(II), Al(III), Mn(II), Fe(II), Fe(III), Ni(II), Zn(II). The D-values for these cations have been determined in acetic acid ammonium oxalate medium using cation exchange Amberlite IR-120 in NH_4^+ form and anion exchanger Amberlite IRA – 400 in Cl^- form. The batch equilibration method was employed for the determination of the distribution coefficients (D-Values). The results were

discussed the composition of the various complex species present in the resin and solution phases of the various complex species present in the resin and solution phases were established by the treatment of equilibrium functions. Considering the chemical interactions and the buffering action of the medium, the sorption behaviour of the charged species was proposed and the mechanism of the exchange process has also been explained.

EXPERIMENTAL

Material

(A) Metal ion Solution :- Stock solution (0.1 M) of Mg(II) Al(III), Fe(II), Fe(III), Mn(II), Ni(II), Zn(II) were individually prepared in double distilled water from their chlorides, nitrates, sulphates and to suppress the hydrolysis of metal solution an appropriate amount of suitable acid was added. All the salts were used either of B. D.H., E. Merck, S. Merck, G. R., Alfa AnalaR, Loba Chem or Harrington Brothers (London) make. The stock solutions were standardized by the methods summarized in Table 3.1.

Table:-3.1 STANDARDIZATION TABLE OF METALS BY EDTA TITRATIONS

Metal ion	Titration Type	pH	Buffer	Indicator ^a	Reference
Mg (II)	Direct ^b	10	Aq NH ₃ / NH ₄ Cl	EBT	25, 44
Al (III)	Back	7-8	Aq NH ₃	EBT	94
Ca (II)	Direct	12	NaOH	MTB	94
	Direct	pH>12	NaOH	M	44
	Replacement ^c	10	Aq NH ₃ / NH ₄ Cl	EBT	94
Mn (II)	Direct ^d	10	Aq NH ₃ / NH ₄ Cl	EBT	44, 94
Fe (III)	Direct ^e	2-3	Dil HNO ₃ KSCN- NaCH ₃ COO		94
	Direct	2-3	KCl – HCl	NH ₄ Cns	94
	Back	4-5	HCl /CH ₃ COONa	PAN	17,18,25,27
	Direct	2-3	Dil HNO ₃	VB	94

Co (II)	Direct	7-10	Aq NH ₃ / NH ₄ Cl	EBT	
	Direct	6		M	44
	Back	5	HCl /CH ₃ COONa	PAN	25
Ni(II)	Direct	7-10	Aq NH ₃ / NH ₄ Cl	M	44,94
	Back	5	HCl /CH ₃ COONa	PAN	25
Cu (II)	Direct	7-10	Aq NH ₃ / NH ₄ Cl	M	44,94
Zn (II)	Direct	10	Aq NH ₃ / NH ₄ Cl	EBT	25, 44, 94
Ag (I) as AgCl	Indirect (Using K ₂ [Ni(Cn) ₄])	10	Liq NH ₃ / 1 M NH ₄ Cl	M	94
	Argentometry	-	Mohr method Volhard Method	K ₂ CrO ₄ NH ₄ SCN	94
Cd (II)	Back	5	HCl /CH ₃ COONa	PAN	25
	Direct	10	Aq NH ₃ / NH ₄ Cl	EBT	44
La (III)	Back	5	HCl /CH ₃ COONa	PAN	25
Hg (II)	Direct	6	Hexamine / HNO ₃	X.O.	94
Pb (II)	Direct	6	Hexamine / HNO ₃	X.O	94
	Direct	-	NH ₃	MTB	44
Th (IV)	Direct	2-3	Dil HNO ₃	XO	94

a : EBT : Eriochrome Black T, MTB : Methyl Thymol Blue, PAN : 1- (2 – pyridilazo) – 2 Nappthol, VB : Variamine Blue, M: Mureoxide, XO : Xylenol Orange ; b : warming optional ; C : Mg EDTA complex was added before the addition of buffer ; d : a pinch of ascorbic acid (Glaxo, uncoated celin tablets of Vitamin C) was added before the addition of buffer; e : Performed at 40°C.

(B) Ammonium Acetate (NH₄OAc) solution: - 1.0 M of NH₄OAc(E. Merck G. R.) was prepared by dissolving the salt in the water and was standardized by the determination of ammonium content(106).

(C) Oxalic Acid (OXAc) solution: - 0.1 M stock solution of oxalic acid (E-merck) was prepared in water and was standardized by standard method.

(D) Acetic Acid (AcOH) solution: - 5.0 M stock solution of Acetic acid was prepared by diluting with water and was standardized by standard method.

(E) Buffer Solutions: -

(i) **pH -10 :-** A buffer of pH – 10 was prepared by dissolving 70.0gm of NH_4Cl in 570ml of liquor ammonia (Glzxo Analar sp.gr. 0.90) and then diluted with water to one litre(106).

(ii) **Ph-5 :-** A buffer of pH -5 was prepared by dissolving 27.3g. of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in water containing 60 ml of 1N HCl and then diluted with water to 1 liter (106)

(iii) **Ph-2.2: -** A buffer of pH– 2.2 was prepared by 0.2 m of KCl solution taken 50 ml & 0.2 m of HCl solution taken 6.7 ml & mixed it & then diluted with water to 200 ml (106).

(iv) **pH 4 & 6:-** A buffer of pH 5.0 & 6.0 were prepared by adding desired volumes of 30% aqueous solution of hexamine and then adjusting the pH with the help of pH meter highly diluted HNO_3 was used to have exact pH range (106).

Other desired pH ranges were obtained by maintaining the pH of the solution of the addition of a suitable quantity of acid or alkali and monitoring with the help of a pH meter. The pH indicator papers (B.D.H) were also employed to check the pH of the solution in some cases during titration and when necessary.

(F) Indicators :-

(i) **Eriochrome black T or ErioT (EBT): -** was prepared by grinding the sample (B.D.H.) base ($\text{EBT}:\text{NaCl}$; 1:25) to a very fine powder

(ii) **Xylenol orange (XO): -** was prepared by grinding this dye (LOBA, G. R.) in Potassium nitrate (B.D.H., A. R.) Base ($\text{XO}:\text{KNO}_3$, 1:20) to a very fine powder.

(iii) **Methyl thymol Blue (MTB): -** was prepared by grinding the dye (Loba G. R.) in potassium nitrate base (B.D.H. Analr) ($\text{MTB}:\text{KNO}_3$ -1:100) to a very fine powder(2).

(iv) **Mureoxide: -** was prepared by grinding the dye (BDH-AR) in potassium nitrate base (Mureoxide KNO_3 , 1:100) to a very fine powder(2).

(v) **Potassium thiocyanate :-** Sodium acetate mixtures were used as such in titration of iron (iii)(2).

(vi) 1-(2-Pyridilazo)-2 naphthol(PAN) indicator :- 0.05% solution of PAN (E. Merck) was prepared in absolute ethanol(2).

(vii) Mg-EDTA Complex solution: - The equimolar complex solution was prepared by mixing equal volumes of 0.1 M magnesium sulphate solution with 0.1 M EDTA solution. An appropriate amount was prepared and stored in polythene bottle (106).

(viii) Indicators used in Argentometry: - (i) 5% K_2CrO_4 aqueous solution (Mohr method) (ii) 0.1 M NH_4SCN aqueous solution (Volhard method) (106).

(G) Resins :-

(i) Cation Exchange Resin:- Strongly acidic BDH Analytical grade cation exchanger Amberlite IR-120 (16-50 mesh, - 8% of crosslinking) in NH_4^+ - form was used usually the resin is supplied in the H^+ - form but it always associated with unwanted materials like dead resin portions, adsorbed preparatory organic compounds and the heavy metal ions etc. Therefore, it needs pre standardization, which was followed in a number of steps. In common practice the resin slurry is transferred in the column and the resin bed is treated with 2.0 M EDTA solution with a optimum speed to remove unwanted heavy metal ions. A column was than washed with water followed by its illusion with 2.0 M NaOH and 2M HCl solutions alternatively and finally with water till the effluent is free from H^+ and Cl^- . The resins thus obtained were air-dried and than its capacity were determined by standard method.

For these experiment the resin was required in the NH_4^+ from, therefore, if was converted to NH_4^+ -form using an excess of 2.0M ammonium chloride as eluting agent. Finally a drop of the effluent solution was checked by litmus paper for the presence of acid on getting negative acid test by litmus paper the washing were done with water till column be come free from chloride ion. Now the NH_4^+ -form converted resin was transferred to a sintered glass filter fitted with the suction jar air-drying. The resin thus prepared was stored in a well-closed bottle. Again its capacity was checked and which was found in accordance to the capacity what was determined for H^+ -form. Its moisture contained was also determined and was found 32% or 0.32g per g of air-dried resin.

(ii) **Anion Exchange Resin:** - The commercially supplied resin, Amberlite-IRA-400 (mesh 50 -100 , 8% of cross linkage) was used after pre standardization as mentioned under cation exchanger resin had. It was also standardized for its capacity and the moisture contained which was found 23.8%.

(H) Instrument: -

pH – Meter :- A main operated Orion Research Microprocessor ion analyser/901 and accessories having glass and calomel electrode assembly were employed for pH measurements. The indicator operated on 220 volts/50 cycles stabilized AC mains. The scale was standardized and checked frequently using buffer solution supplied by the same manufacture.

CATION EXCHANGE STUDIES

Resin Capacity :- Accurately weighed quantity (1.0g, 2.0g, 3.0g, 4.0g, and 5.0g) of the cation exchanger (Amberlite IR-120 in NH_4^+ - form) was transferred in a column by making a survey with water excess of ca. 2M HCl solution. In case of H^+ -form resin, the H^+ content was estimated by totally converting the resin into the Na^+ form using 2M NaNO_3 , while for NH_4^+ – form resin 2M NaOH was used and the conversion experiments was performed in a beaker instead of using elution methodology. Accordingly the subsequent steps were followed to determine the capacities of these resins in different forms as well as their present moisture contents.

Table - 3.2: Determination of Resin Capacity by Column experiment: Amberlite IR-120 (NH_4^+ – form, mesh, 8-10% of cross linking) Eluting Agent – 20.0%NaCl

Amount of resin	Total Diluted Vol. Of H^+ Effluent	Total Vol. Of (M/20) NaOH used for 25 mL of H^+ Effluent (mL)	Correspondin g vol. Of Total H^+ Effluent Vol (mL)	Capacity =(av/w) in milli equivalent of H^+ /g of Resin
1.0	100.0	8.6	43.2	2.72meq/g
2.0	100.0	17.7	88.4	2.76meq/g
3.0	250.0	10.6	132.0	2.75meq/g
4.0	250.0	14.1	176.0	2.75meq/g
5.0	250.0	17.6	220.0	2.75meq/g

DISTRIBUTION STUDIES

Determination of distribution coefficient (D) was carried out by the batch equilibrium technique. Aqueous phase mixture solutions were having the equimolar ratio of $4.0 - 9.0 \times 10^{-3}M$ of both NH_4OAc and oxalic acid and of metal ions fixed to $3.0 \times 10^{-3}M$. After the mixing of these solutions 1.000g of air-dried resin NH_4^+ - form was added. The flasks were shaken mechanically for 3 hours to ensure the complete equilibrium. It was ascertained that this duration was adequate to attain the equilibrium. There after the resin was filtered off and the metal ion content was determined in an aliquot of the filtrate by titrating again EDTA. And Distribution coefficient (D) and correspondence of loading values (Table 3.3) were calculated using the relations.

$$D = \frac{\text{Meq. of the metal g of resin}}{\text{Meq. of the metal ion per mL of solution}} \text{ and } L(\%) = \left[\frac{D}{(V + D)} \right] \times 100$$

All experiments were carried out at least in duplicate by repeating the full set and average values, for conceding data have been taken otherwise the set was again repeated. The relative experimental errors in the determinations of the D values were within the limits of 2-5% for D-values between 10 and 1000, but are higher for very low coefficients.

Table-3.3: Values of Distribution Coefficient (D) of NH_4OAc – $OXAc$ media
($AcOH = 0.25M$) of Amberlite IR- 120 (NH_4^+ – form)

Concentration of $[OX] \times 10^3$	Distribution Coefficient of Metal Ion $[3.0 \times 10^{-3}]$						
	Mg(II)	Al(II)*	Mn(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)**
4.00	400.0	186.0	130.7	1363.4	552.2	408.4	400.0
4.25	310.0	200.0	122.5	1283.8	510.7	365.3	355.9
4.50	233.3	216.6	114.3	1204.3	469.2	328.9	310.9
4.75	187.0	233.3	110.5	1137.6	413.9	297.8	272.5
5.00	150.0	254.1	100.0	1071.8	358.7	271.0	233.3
5.25	119.0	275.0	96.5	1019.7	332.5	247.8	205.5
5.50	106.8	301.7	88.5	967.6	306.3	227.4	177.7
5.75	78.0	328.5	80.7	922.3	276.5	209.6	163.8
6.00	66.6	364.2	71.4	877.1	246.8	193.8	150.0
6.25	54.0	400.0	68.1	838.5	224.6	179.8	132.1
6.50	41.5	450.0	64.9	800.9	202.4	167.3	114.2

6.75	84.0	500.0	53.8	768.5	185.2	156.1	257.1
7.00	150.0	575.0	42.8	737.9	168.1	146.0	400.0
7.25	257.1	650.0	36.8	709.8	154.0	136.9	P
7.50	400.0	575.0	30.4	681.7	140.7	128.6	P
7.75	P	500.0	30.4	656.7	128.6	121.1	P
8.00	P	450.0	30.4	631.7	116.5	114.2	P
8.25	P	364.2	30.4	610.6	108.5	108.0	P
8.50	P	328.5	30.4	589.6	100.0	102.2	P
8.75	P	301.7	30.4	569.8	100.0	96.9	P
9.00	P	275.0	30.4	550.6	100.0	92.0	P

P = precipitate

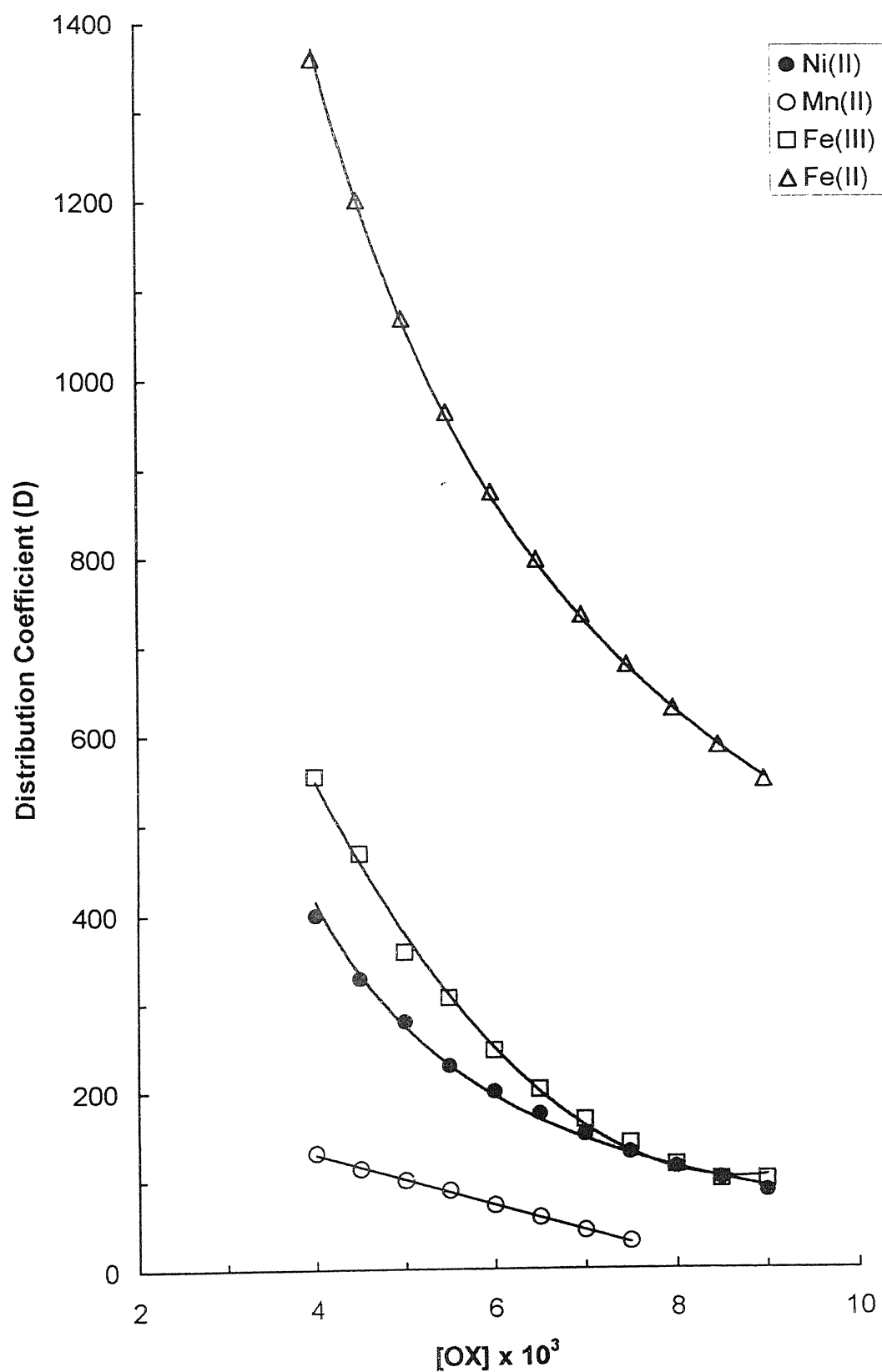
* = Reading taken from 3.0×10^{-3} up to 13×10^{-3} M of [OX] concentration see in discussion

** = Reading taken from 3.25×10^{-3} M of [OX] concentration see in discussion

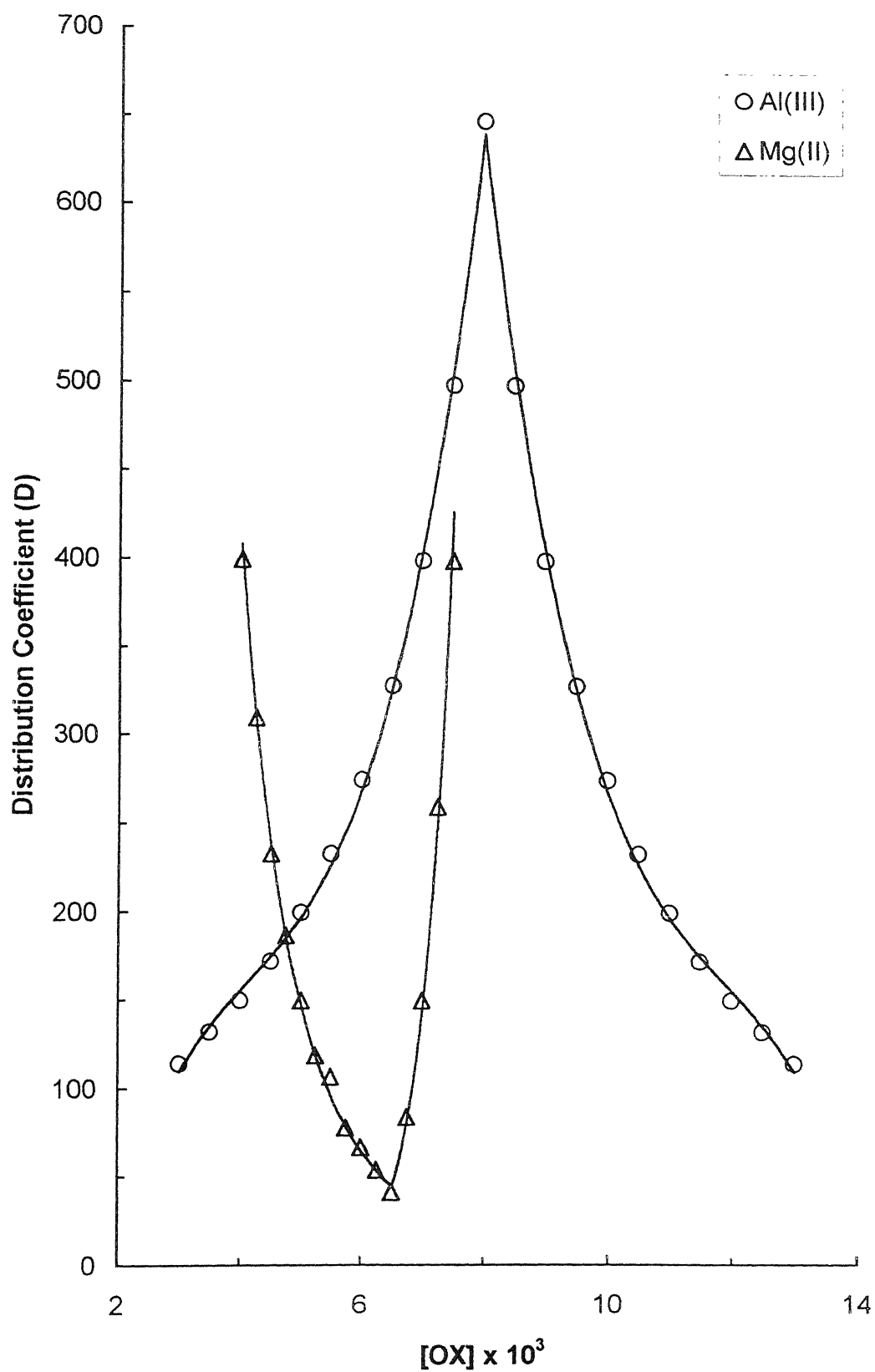
Table-3.4: Values of Percentage Loading (L%) of NH_4OAc – OXAc media
($\text{AcOH} = 0.25\text{M}$) of Amberlite IR- 120 (NH_4^+ – form)

Concentration of [OX] $\times 10^3$	Percentage Loading (L%) Metal Ion [3.0×10^{-3}]						
	Mg(II)	Al(II)*	Mn(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)**
4.00	80.0	61.7	56.7	93.2	84.7	80.3	80.0
4.25	75.6	63.3	55.1	92.8	83.6	78.5	78.1
4.50	70.0	65.0	53.3	92.3	82.4	76.7	75.7
4.75	65.2	66.7	52.5	91.9	80.5	74.9	73.2
5.00	60.0	68.4	50.0	91.5	78.2	73.0	70.0
5.25	54.3	70.0	49.1	91.1	76.9	71.2	67.3
5.50	51.6	71.8	46.9	90.6	75.4	69.5	64.0
5.75	43.8	73.3	44.7	90.2	73.4	67.7	62.1
6.00	40.0	75.1	41.7	89.8	71.2	66.0	60.0
6.25	35.1	76.7	40.5	89.3	69.2	64.3	56.9
6.50	29.3	78.5	39.4	88.9	66.9	62.6	53.3
6.75	45.7	80.0	35.0	88.5	64.9	61.0	72.0
7.00	60.0	81.8	30.0	88.1	62.7	59.4	80.0
7.25	72.0	83.3	26.9	87.7	60.6	57.8	P
7.50	80.0	85.2	23.3	87.2	58.5	56.3	P
7.75	P	86.7	23.3	86.8	56.3	54.8	P
8.00	P	85.2	23.3	86.3	53.8	53.3	P
8.25	P	83.3	23.3	85.9	52.0	51.9	P
8.50	P	81.8	23.3	85.5	50.0	50.5	P
8.75	P	80.0	23.3	85.1	50.0	49.2	P
9.00	P	78.5	23.3	84.6	50.0	47.9	P

**Fig. 3.1 Distribution Coefficient (D) vs [OX]
For Amberlite IR-120**



**Fig. 3.2 Distribution Coefficient (D) vs [OX]
For Amberlite IR-120**



**Fig. 3.3 Distribution Coefficient (D) vs [OX]
For Amberlite IR-120**

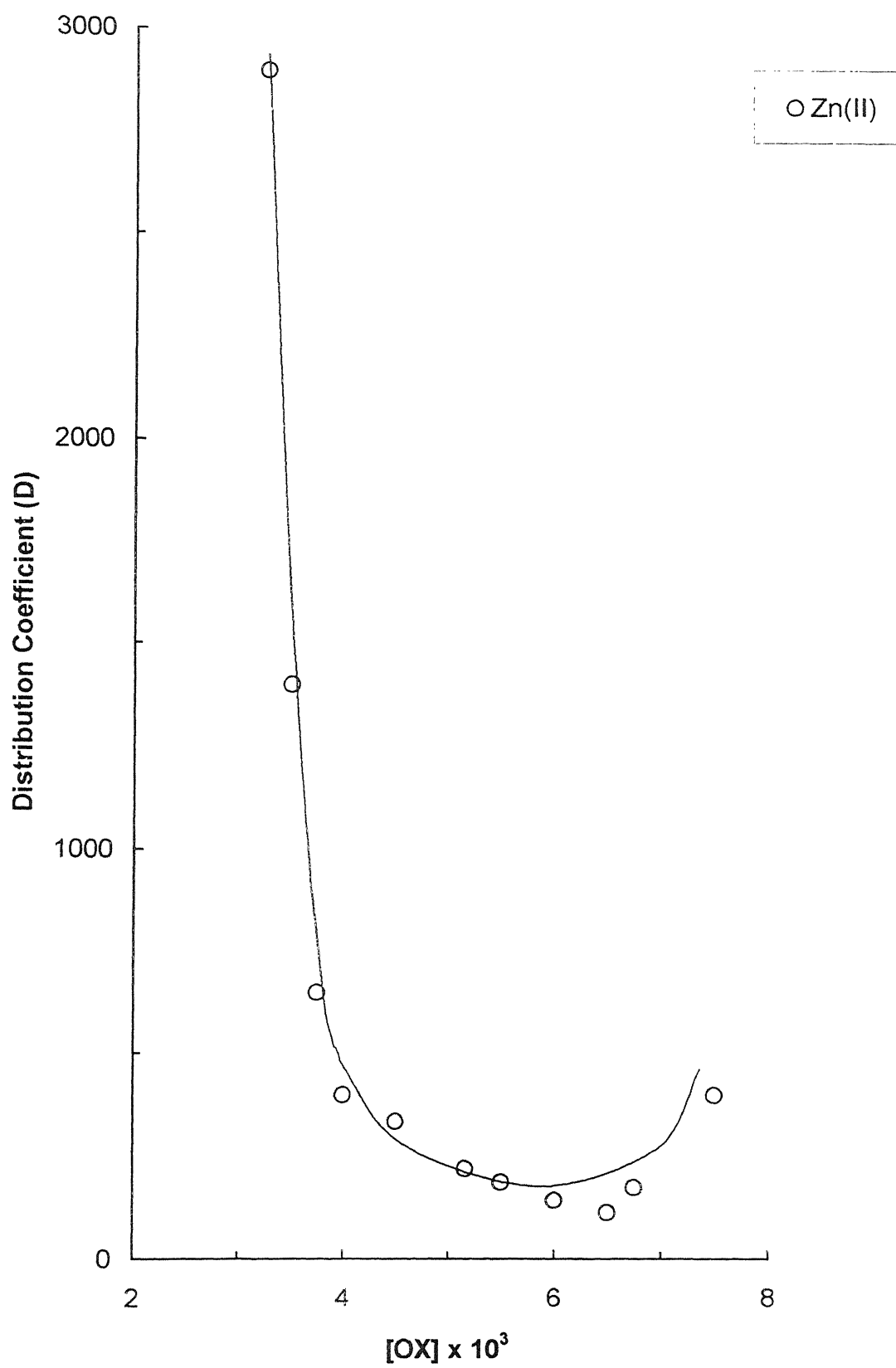
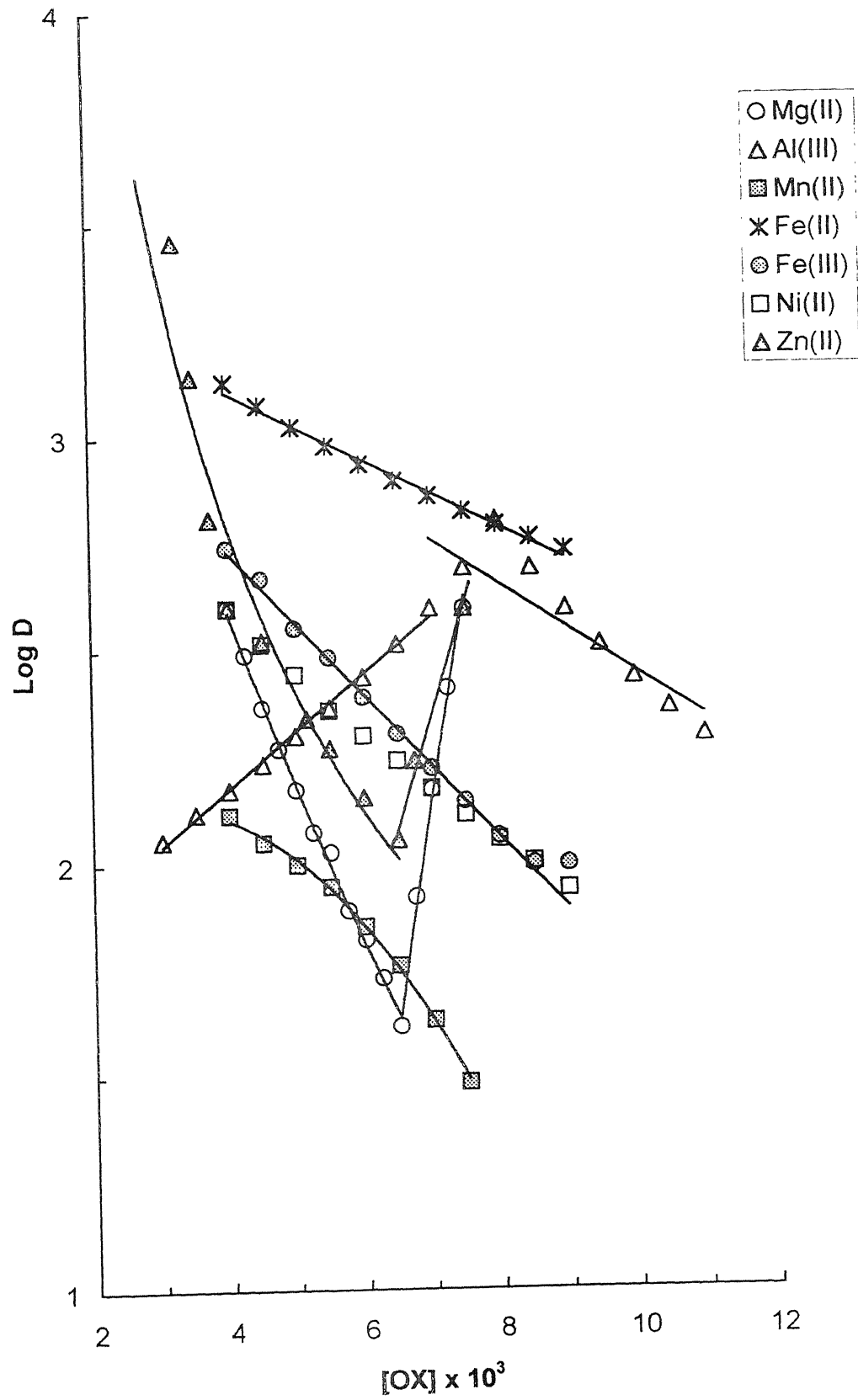
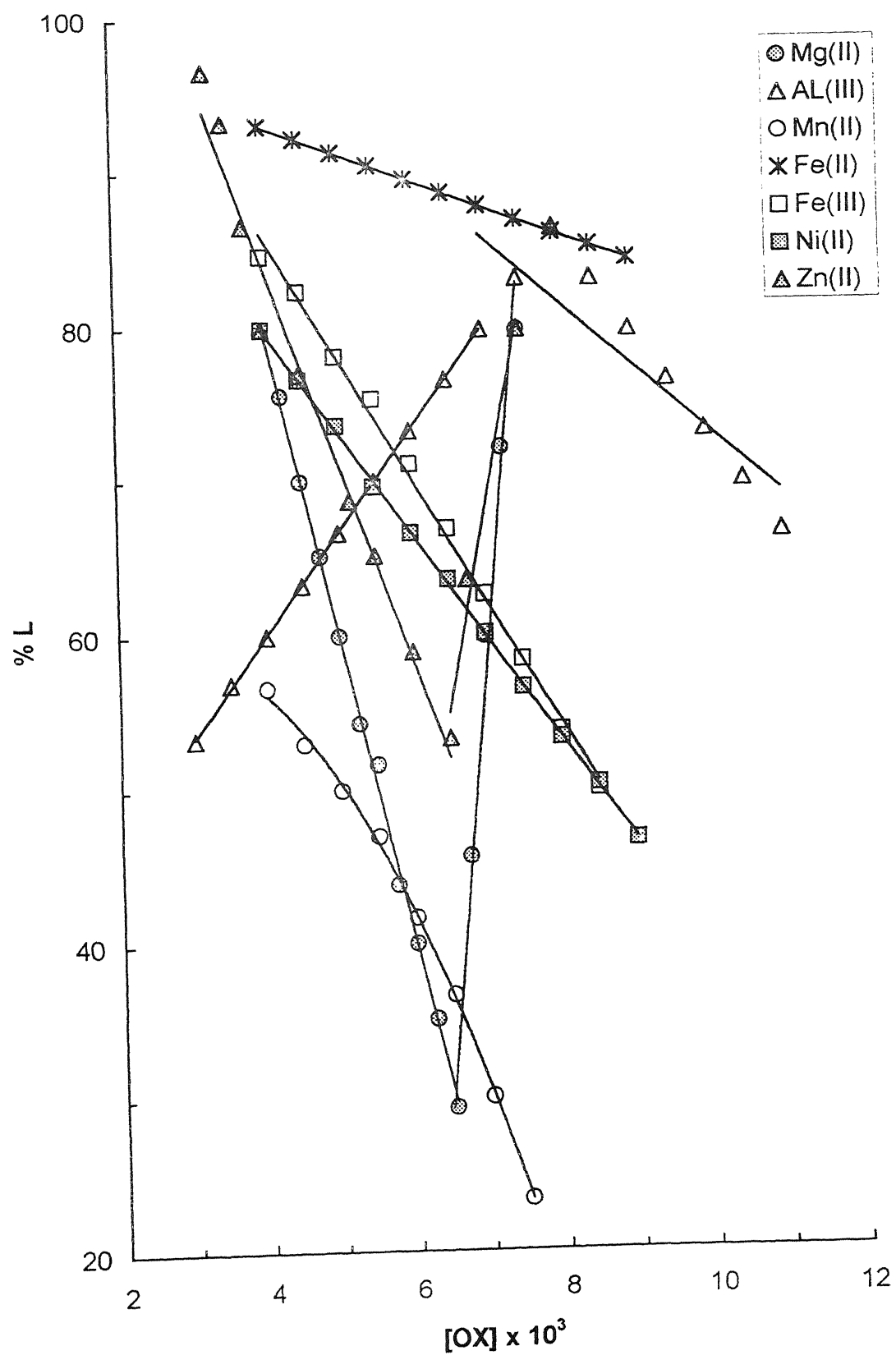


Fig. 3.4 Log D vs [OX] For Amberlite IR-120



**Fig. 3.5 Percentage Loading(%L) vs [OX]
For Amberlite IR-120**



P = precipitate

* = Reading taken from 3.0×10^{-3} up to 13×10^{-3} M of [OX] concentration see in discussion

** = Reading taken from 3.25×10^{-3} M of [OX] concentration it see in discussion

RESULT AND DISCUSSION

The distribution coefficient (D) values as evaluated from experimental data are given in table 3.1. Each batch equilibrium experiment was performed at least in duplicate, but all other experiments, which were found, not following a usual trend, then the experiments were repeated sometimes 4 – 5 times to check the validity and to conclude, correct information. The general steps of errors associated to normal laboratory working are the errors originated due to estimation methods of the various metal ions. The other main source of errors are inhomogeneity of the resin, the uncertainty of water content of the air dried resin and the analytical errors.

Generally D-values determined at relatively higher resin loading, as in these experiments, provide more practical results than at tracer concentrations, because the error due to secondary effects like sorption by the walls of the vessels, are not significant. The corresponding loading values are summarised in table 3.2. The plots of metal ion D-values vs [OX] and %L Vs [OX] are given in fig. 3.1, 3.2 and 3.3 and 3.4, 3.5 respectively.

The cation exchange behaviour of the individual metal ions indicates the sorption trends are not following a well-defined decreasing or increasing pattern in selected concentration range of $\text{NH}_4\text{OAc-OXAc}$ mixture. On the basis of experimentally established observations, the investigated metal ions are varying in their exchange behaviours. The metal ions Ca(II) , Cd(II) , Cu(II) , Co(II) , La(III) , Pb(II) , Th(II) , which were tried in these media could not be studied due to either insolubility of their oxalates probably formed in selected mixed solutions of $\text{NH}_4\text{OAc-OXAc-AcOH}$ or due to formation of their hydrolytic species causing precipitation

Metal ions Mn(II) , Fe(II and III) , Ni(II) had shown a gradual decrease indicating involvement of these metal ions in the complexation activities leading to gradual poor uptake due to decrease in free metal ion concentration as well as cationic complex species. While the D-plots of Ni(II) , Fe(II and III) are curved but

Mn(II) is straight line. It is clearly showing that the displacement of coordination water is varying metal to metal and consequently the complexation equilibrium is affected and this may be responsible for obtaining curves of similar nature instead of deviated behaviour of these metal ion (Ni(II), Fe(II and III))plots. The displacement of coordination water in Mn (II) is so that it is resulted to a straight line. The other important factors, which are definitely playing significant role in these observed deviation of the sorption tendencies (of the studied metal ions), may be linked with the activities of other various species present on these systems. All ionic species not only affecting the metal ion charge and its concentration impact, but they are solubilizing the ion exchange distribution equilibrium of the studied metal ions similarly the various unavoidable thermodynamic considerations are simultaneously contributing to the metal complexation equilibria as well as respective ion exchange equilibria putting the gross effect on the metal distribution between the solid resin and aqueous solution phases.

Mg(II) shows a very unique sorption behaviour, i.e., its sorption not following the usual trend instead the higher sorption(42) is observed at 4.00×10^{-3} equimolar OXAc-NH₄OAc mixture (constant 0.25M CH₃COOH) solution with a D-values=400.0. A gradual decrease observed at 6.25×10^{-3} equimolar mixture solution and then again the D-values are showing enhancement up to 7.50×10^{-3} equimolar solution with same D-value. It has also been observed that at lower concentration of 3.75×10^{-3} equimolar mixture solution, and at higher concentration of 7.75×10^{-3} equimolar mixture solution, experiments could not be performed because of the occurrence of precipitation indicating the dominance of species having neutral charge.

The gradual decrease from highest D-value 400 to 41.5 cannot be simply explained by considering the usual complexation considerations. The medium contains cations H⁺ and NH⁺ apart the metal ion Mg²⁺ and the anions, C₂O₄²⁻, CH₃COO⁻ and a little SO₄²⁻ (corresponding to Mg⁺). The oxalate and the acetate may be participating in the complexation or interaction with the magnesium as well as with the cations NH₄⁺ and H⁺, which are also taking part in the competitive sorption with the magnesium. The sorption equilibrium is so shifted that first the uptake of magnesium is decreasing but after reaching to a lowest value it starts increasing showing definitely change in the nature of sorbable species or the competitive

sorption tendencies of H^+ and NH_4 now no more so effective may be due to the buffering effect of the medium. Therefore their sorption is suppressed as well as the buffering and solvalization of the medium also appears some way affecting so that the complexation of Mg with oxalate and the acetate is also decreased rather the complex species are disproportionating resulting to increase of free Mg^{2+} or cationic magnesium species which are sorbing and causing again enhancement in the D value of magnesium.

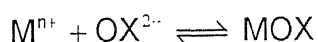
Zn(II) also showing to some extent the similar type of behaviour like Mg(II)(16). But may not be exactly like Mg(II) and only at the last three concentrations before the precipitation starts an increase has been observed as indicated by enhancement of the D values. One can conclude like magnesium same equilibria and buffering as well as solvalization are responsible for this trend of sorption of Zn(II) in the investigated range of equimolar oxalic acid and ammonium acetate mixture solutions. Zinc is a last member of the first transition series (may not be considered by definition a transition element) and definitely possesses a different or relatively a strong complexing nature than Mg and the observed little deviation in its sorption may be contributed by this inherent transitory factor.

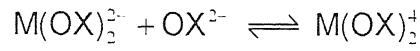
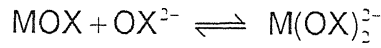
The case of Al (III) is just reverse of the Mg (II) which is also a very unique and abnormal behaviour observe in these investigated media, Al(III) is showing gradual enhancement in the D value with the increase of equimolar oxalic acid - ammonium acetate mixture solutions. This is a very rare and unusual sorption behaviour shown by the Al(III) i.e. instead by complexation D values should decrease, these are increasing upto D value 650 then they start decreasing to D value 150 (same as initial D value). This anomalous sorption of Al may be explained by assuming the hydrolytic behaviour of Al^{3+} is stronger at lower range of equimolar mixture solution, which is showing suppressing, by gradual complexation by oxalate (34,35) or acetate (33,108) on increasing the equimolar mixture solution concentrations. The overall effect by these two equilibria leaving such cationic Al^{3+} species which are relatively not that bulky and therefore, able to be sorbed on the exchanger more strongly resulting enhancement to the D – value, but these equilibria may gradually be suppressed or the complexation equilibrium starts dominating at further higher equimolar mixture solution concentrations causing

gradual decrease in D – values. Like Mg(II) the behaviour of Al(III) is just reverse but it doesn't mean that the complexation tendencies, the hydrolytic nature and the competitive sorption affinities etc. are also reverse. Actually the degree of hydrolysis, complexation, sorption, buffer action, solvalization and the gross effects of all these as well as the other factors are in the usual manner, but these are shifted either by the effect of the metal ion Mg or Al in the selected concentration range of the equimolar mixture solutions or the formation of the charged species in the medium, and so that the partition of the concerned metal with respect to its sorption affinity for Al(III) is inverted to Mg(II) or vice versa, Al(III) has not showing precipitation at any stage of the investigated media.

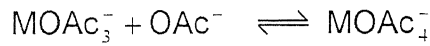
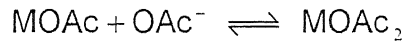
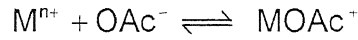
Considering the oxalato equilibrium is relatively more dominating and effective though acetate is playing (24,8) an important role especially responsible for enhancement of the solubility of oxalato species. It may not be incorrect to presume that in the investigated range of the equimolar mixture solution neither pure metal oxalato nor pure metal acetato species are forming but it appears that the existing complex species are carrying the mixed type complexing nature having both the oxalate and acetate ions in the coordination sphere. This mixed complexation by the oxalate and acetate overall not affecting the charge on the respective species because of the symmetric arrangements, therefore the effective distribution of the metal with respect to charge is not changing while the other factors like the overall size of the complex species has definitely differed which is consequently affecting the overall metal ion distribution, i.e., causing the variation in the D values.

The complexation aspects of these metal – oxalic acid – ammonium acetate systems have also been discussed in the light of equilibrium formation constants of metal ions using Shubert's approach of evaluating the stability constants by ion exchange. Due to limited scope of the ion exchange method it can not be applied to evaluate the stability (formation) constants of the mixed ligand systems. So in present studies the stability (formation) constants are calculated considering only the oxalate interaction and values thus obtained are relative to acetate and species present in the solution, and the respective equilibria may be given as,





Similarly, the calculation were also carried out by considering the acetate interaction with respective to oxalate, and there equilibria may be represented as,



and the equilibrium constants are given as,

$$K_1 = \frac{[\text{MOx} / \text{OAc}]}{[\text{M}][\text{Ox} / \text{OAc}]} \quad \text{—————} \quad (1)$$

$$K_2 = \frac{[\text{M}(\text{Ox} / \text{OAc})_2]}{[\text{MOx} / \text{OAc}][\text{Ox} / \text{OAc}]} \text{ or } \beta_2 = \frac{[\text{M}(\text{Ox} / \text{OAc})_2]}{[\text{M}][\text{Ox} / \text{OAc}]^2} \quad \text{—————} \quad (2)$$

$$K_n = \frac{[\text{M}(\text{Ox} / \text{OAc})_n]}{[\text{M}(\text{Ox} / \text{OAc})_{n-1}][\text{Ox} / \text{OAc}]} \text{ or } \beta_n = \frac{[\text{M}(\text{Ox} / \text{OAc})_n]}{[\text{M}][\text{Ox} / \text{OAc}]^n} \quad \text{—————} \quad (3)$$

The overall or gross metal ion exchange distribution for various bivalent metal ion species may be represented as (considering the maximum association of the ligand, i.e. value of n=3)

$$D = \frac{[\text{M}]_r}{[\text{M}] + \beta_1 [\text{M}][\text{L}] + \beta_2 [\text{M}][\text{L}]^2 + \beta_3 [\text{M}][\text{L}]^3} \quad \text{—————} \quad (4)$$

$$D = \frac{[\text{M}]_r}{[\text{M}]} \left(\frac{1}{1 + K_1 [\text{L}] + \beta_2 [\text{L}]^2 + \beta_3 [\text{L}]^3} \right) \quad \text{—————} \quad (5)$$

The factor $[\text{M}]_r/[\text{M}]$, is the distribution coefficient of metal species in absence of the ligand, and is usually designated as D_o (i.e., distribution coefficient of free metal ion species), then,

$$\frac{D_o}{D} = 1 + \sum_{n=1}^{N=n+3} \beta_n [L]^n \quad (6)$$

$$\frac{(D_o/D - 1)}{[L]} = K_1 + \beta_2 [L] + \beta_3 [L]^2 \quad (7)$$

$$\frac{\{(D_o/D - 1)/[L]\} - \beta_1}{[L]} = \beta_2 + \beta_3 [L] \quad (8)$$

The value of K_1 , and on knowing the value of β_1 , from equation (7), the values of β_2 and β_3 are obtained as the intercept or the limiting value of the curve $\{(D_o/D - 1)/[L]\}$ vs $[L]$ and $\frac{\{(D_o/D - 1)/[L]\} - \beta_1}{[L]}$ vs $[L]$ (Fig.3.6,3.7,3.8 and 3.9) Table 3.5, 3.6, 3.7, 3.8, 3.9, 3.10,3.11.

Table- 3.5 Shubert's Function and Other Calculated Variables of Mg(II) in mixed $\text{NH}_4\text{OAc} - \text{OXAc}$ media ($[\text{AcOH}] = 0.25\text{M}$) on Amberlite IR -120(NH_4^+ -form)

$[\text{OX}]\text{M} \times 10^3$	D	$\{(D_o/D) - 1\}$	$(D_o/D - 1)/[\text{OX}] \times 10^{-4}$	$(D_o/D - 1) - \beta_1 / [\text{OX}]^2 \times 10^{-6}$
4.0	400.0	59.2	1.5	2.18
4.5	233.3	102.3	2.3	2.11
5.0	150.0	159.6	3.2	2.08
5.5	106.8	224.4	4.1	2.06
6.0	66.6	318.5	5.3	2.09
6.5	41.5	447.1	6.9	2.17
7.0	150.0	159.6	2.3	1.36
7.5	400.0	59.2	0.8	1.07

Table- 3.6: Shubert's Function and Other Calculated Variables of Al(III) in mixed $\text{NH}_4\text{OAc} - \text{OXAc}$ media ($[\text{AcOH}] = 0.25\text{M}$) on Amberlite IR-120(NH_4^+ -form)

$[\text{OX}]\text{M} \times 10^3$	D	$\{(D_o/D) - 1\}$	$(D_o/D - 1)/[\text{OX}] \times 10^{-4}$	$(D_o/D - 1) - \beta_1 / [\text{OX}]^2 \times 10^{-5}$
3.00	114.2	89.09	2.97	119.3
3.50	130.7	76.88	2.20	80.2
4.00	150.0	67.59	1.69	57.5
4.50	172.2	58.72	1.30	42.5
5.00	200.0	50.44	1.01	32.4
5.50	233.3	43.09	0.78	25.3
6.00	275.0	36.41	0.61	20.3

6.50	328.5	30.31	0.47	16.5
7.00	400.0	24.72	0.35	13.7
7.50	500.0	19.58	0.26	11.6
8.00	650.0	14.83	0.19	9.9
8.50	500.0	19.58	0.23	9.9
9.00	400.0	24.72	0.27	9.8
9.50	328.5	30.31	0.32	9.8
10.0	275.0	36.41	0.36	9.7
10.5	233.3	43.09	0.41	9.7
11.0	200.0	50.44	0.46	9.7
11.5	172.2	58.72	0.51	9.7
12.0	150.0	67.59	0.56	9.8
12.5	130.7	76.88	0.62	9.8
13.0	114.2	89.25	0.69	10.0

Table- 3.7: Shubert's Function and Other Calculated Variables of Mn(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OX]M x 10 ³	D	{(D ₀ /D)-1}	(D ₀ /D-1)/[OX] x 10 ⁻²	(D ₀ /D-1)-β ₁ / [OX] ² x 10 ⁻⁵
4.00	1.31	0.86	2.15	1.55
4.50	1.13	1.16	2.57	1.37
5.00	1.00	1.43	2.86	1.24
5.50	8.87	1.74	3.17	1.13
6.00	7.14	2.40	4.01	1.03
6.50	6.48	3.21	4.94	0.95
7.00	4.29	4.67	6.67	0.89
7.50	3.04	6.99	9.32	0.83

Table- 3.8: Shubert's Function and Other Calculated Variables of Fe(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OX]M x 10 ³	D	{(D ₀ /D)-1}	(D ₀ /D-1)/[OX] x 10 ⁻²	(D ₀ /D-1)-β ₁ / [OX] ² x10 ⁻⁴
4.00	1363.4	1.79	4.48	3.64
4.50	1204.3	2.16	4.80	3.95
5.00	1071.8	2.55	5.10	4.15
5.50	967.6	2.93	5.33	4.20
6.00	877.1	3.34	5.56	4.23
6.50	800.9	3.75	5.77	4.23
7.00	737.9	4.16	5.94	4.16

7.50	681.2	4.59	6.11	4.12
8.00	631.7	5.02	6.28	4.07
8.50	589.6	5.45	6.42	3.99
9.00	550.7	5.91	6.57	3.94

Table- 3.9: Shubert's Function and Other Calculated Variables of Fe(III) in mixed NH₄OAc-OXAc media ([AcOH] = 0.25M) on Amberlite IR-120(NH₄⁺-form)

[OX]M x 10 ³	D	{(D ₀ /D)-1}	(D ₀ -D)/[OX] x 10 ⁻³	(D ₀ /D-1)-β ₁ / [OX] ² x10 ⁻⁵
4.00	555.00	3.05	0.76	4.29
4.50	469.25	3.79	0.84	3.99
5.00	358.71	5.26	1.05	4.01
5.50	306.5	6.33	1.15	3.82
6.00	246.82	8.10	1.35	3.84
6.50	202.41	10.10	1.55	3.86
7.00	168.09	12.37	1.77	3.88
7.50	140.77	14.96	1.99	3.93
8.00	116.49	18.29	2.29	4.05
8.50	100	21.47	2.53	4.09

Table- 3.10: Shubert's Function and Other Calculated Variables of Ni(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺-form)

[OX]M x 10 ³	D	{(D ₀ /D) -1}	(D ₀ /D-1)/[OX] x 10 ⁻³	(D ₀ /D-1)-β ₁ / [OX] ² x10 ⁻⁵
4.0	400.00	12.4	3.11	8.25
4.5	328.57	15.3	3.41	8.01
5.0	279.74	18.2	3.64	7.67
5.5	229.67	22.4	4.07	7.75
6.0	200.00	25.9	4.31	7.50
6.5	175.22	29.6	4.56	7.32
7.0	151.04	34.6	4.94	7.33
7.5	130.76	40.0	5.35	7.38
8.0	114.28	46.0	5.75	7.43
8.5	101.34	52.0	6.12	7.43
9.0	87.50	60.4	6.71	7.67

Table- 3.11: Shubert's Function and Other Calculated Variables of Zn(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OX]M x 10 ³	D	{(D _o /D)-1}	{(D _o /D)-1}/[OX] x 10 ⁻⁵	(D _o /D-1)-β ₁ / [OX] ² x10 ⁻⁸
3.00	2900.00	10.5	9.77	2.33
3.25	1400.00	22.8	4.18	0.56
3.50	650.00	50.3	1.77	-0.12
3.75	400.00	82.3	1.01	-0.30
4.00	310.95	106.2	0.70	-0.33
4.50	233.34	141.9	0.47	-0.35
5.00	177.78	186.5	0.32	-0.34
5.50	150.00	239.5	0.23	-0.33
6.00	114.28	290.7	0.18	-0.31
6.50	175.22	189.2	0.26	-0.29
6.75	400.00	82.3	0.58	-0.23

Table:3.12: The calculation of the equilibrium formation constants of the studied metal ions with respect to complexation with oxalate

Metal Ion	D _o	Log k ₁	Log β ₂	Log β ₃
Mg (II)	24097	4.8	6.3	9.6
Al (III)	10288	3.7	6.0	8.0
Mn (II)	243	2.8	5.3	7.8
Fe (II)	3805	2.4	4.6	5.3
Fe (III)	2246	2.9	5.6	7.7
Ni (II)	5373	2.2	5.0	6.9
Zn (II)	33334	5.9	8.0	9.8

The calculations of the equilibrium formation contents of the studied metal ions have also been worked out with respect to complexation with acetate Table 3.13, 3.14, 3.15, 3.16, 3.17, 3.18, 3.19.

Table- 3.13: Shubert's Function and Other Calculated Variables of Mg(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OAc]M	D	{(D _o /D)-1}x10 ⁻⁶	(D _o /D-1)/ [OAc] x 10 ⁻⁷	{(D _o /D-1)/[OAc]- β ₁ }/ [OAc] x 10 ⁻¹⁰
0.2540	400.0	1.41	0.55	13.80
0.2545	233.3	2.41	0.94	13.78
0.2550	150.0	3.75	1.47	13.78
0.2555	106.9	5.27	2.06	13.77
0.2560	75.4	7.46	2.91	13.78
0.2565	53.8	10.5	4.08	13.80
0.2570	150.0	3.75	1.46	13.67
0.2575	400.0	1.41	0.54	13.61

Table- 3.14: Shubert's Function and Other Calculated Variables of Al(III) in mixed $\text{NH}_4\text{OAc} - \text{OXAc}$ media ($[\text{AcOH}] = 0.25\text{M}$) on Amberlite IR-120(NH_4^+ -form)

[OAc]M	D	$\{(D_0/D)-1\} \times 10^{-5}$	$(D_0/D-1)/[\text{OAc}] \times 10^{-6}$	$\{(D_0/D-1)/[\text{OAc}]-\beta_1\}/[\text{OAc}] \times 10^{-8}$
0.25300	114.20	9.11	3.60	5.81
0.25350	132.10	7.88	3.11	5.78
0.25400	150.00	6.94	2.73	5.75
0.25450	172.27	6.04	2.37	5.73
0.25500	200.00	5.20	2.04	5.71
0.25550	233.33	4.46	1.75	5.68
0.25600	275.00	3.78	1.48	5.66
0.25650	328.57	3.17	1.23	5.64
0.25700	400.00	2.60	1.01	5.62
0.25750	500.00	2.08	0.81	5.60
0.25800	650.00	1.60	0.62	5.58
0.25850	500.00	2.08	0.80	5.58
0.25900	400.00	2.60	1.00	5.58
0.25950	328.57	3.17	1.22	5.57
0.26000	275.00	3.78	1.45	5.57
0.26050	233.33	4.46	1.71	5.57
0.26100	200.00	5.20	1.99	5.57
0.26150	172.27	6.04	2.31	5.57
0.26200	150.00	6.94	2.65	5.58
0.26250	132.10	7.88	3.00	5.58
0.26300	114.00	9.13	3.47	5.59

Table- 3.15: Shubert's Function and Other Calculated Variables of Mn(II) in mixed $\text{NH}_4\text{OAc} - \text{OXAc}$ media ($[\text{AcOH}] = 0.25\text{M}$) on Amberlite IR-120(NH_4^+ -form)

[OAc]M	D	$\{(D_0/D)-1\}$	$(D_0/D-1)/[\text{OAc}] \times 10^{-2}$	$\{(D_0/D-1)/[\text{OAc}]-\beta_1\}/[\text{OAc}] \times 10^{-4}$
0.2540	130.8	54.31	2.14	88.13
0.2545	112.8	63.14	2.48	87.99
0.2550	100.0	71.33	2.80	87.85
0.2555	88.67	80.57	3.15	87.72
0.2560	71.42	100.3	3.92	87.62
0.2565	64.83	110.6	4.31	87.49
0.2570	42.85	167.8	6.53	87.54
0.2575	30.43	236.7	9.19	87.64

Table- 3.16: Shubert's Function and Other Calculated Variables of Fe(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OAc]M	D	$\{(D_0/D)-1\} \times 10^{-4}$	$(D_0/D-1)/[OAc] \times 10^{-5}$	$\{(D_0/D-1)/[OAc]-\beta_1\}/[OAc] \times 10^{-7}$
0.25400	1363.4	4.88	1.92	5.77
0.25450	1204.3	5.52	2.17	5.77
0.25500	1071.8	6.21	2.43	5.77
0.25550	967.61	6.87	2.69	5.77
0.25600	877.19	7.58	2.96	5.77
0.25650	800.90	8.30	3.24	5.77
0.25700	737.98	9.01	3.51	5.77
0.25750	681.25	9.76	3.79	5.77
0.25800	631.70	10.5	4.08	5.77
0.25850	589.65	11.3	4.36	5.77
0.25900	550.75	12.1	4.66	5.77

Table- 3.17: Shubert's Function and Other Calculated Variables of Fe(III) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

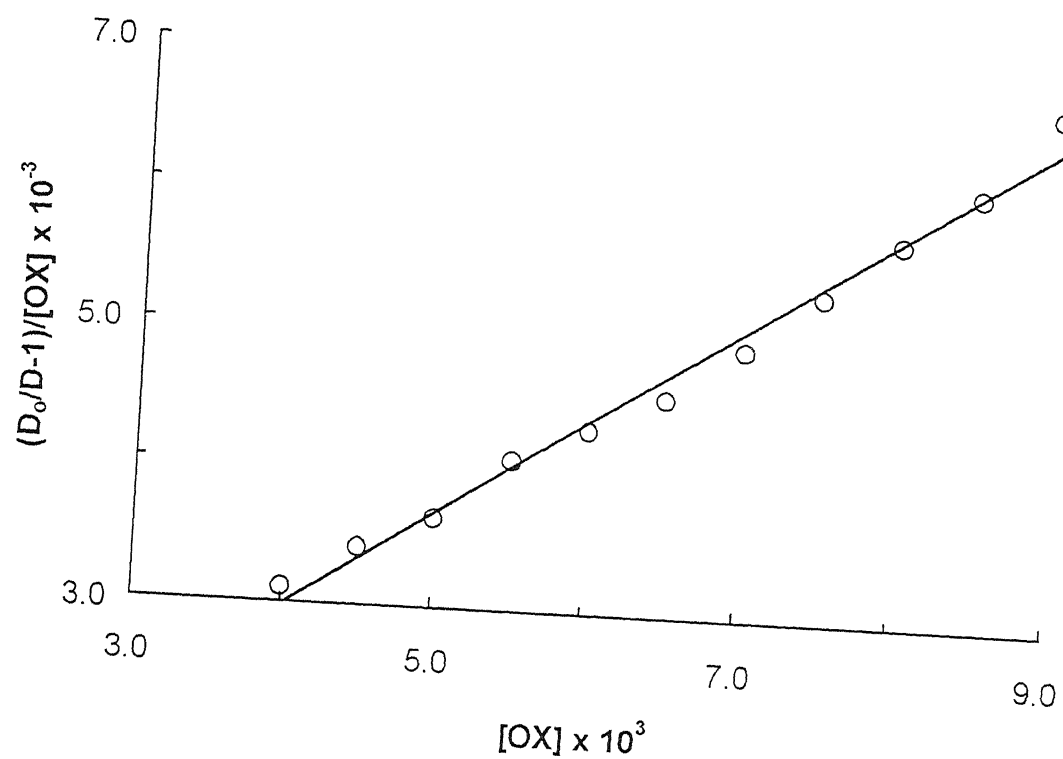
[OAc]M	D	$\{(D_0/D)-1\} \times 10^{-4}$	$(D_0/D-1)/[OAc] \times 10^{-5}$	$\{(D_0/D-1)/[OAc]-\beta_1\}/[OAc] \times 10^{-8}$
0.2540	555.0	8.35	3.29	3.16
0.2545	469.3	9.88	3.88	3.16
0.2550	358.7	12.9	5.07	3.16
0.2555	306.5	15.1	5.92	3.15
0.2560	246.8	18.8	7.34	3.15
0.2565	202.4	22.9	8.93	3.15
0.2570	168.1	27.6	10.7	3.15
0.2575	140.8	32.9	12.8	3.16
0.2580	116.5	39.8	15.4	3.16
0.2585	100.0	46.4	17.9	3.16

Table- 3.18: Shubert's Function and Other Calculated Variables of Ni(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OAc]	D	$\{(D_0/D)-1\} \times 10^{-5}$	$(D_0/D-1)/[OAc] \times 10^{-5}$	$\{(D_0/D-1)/[OAc]-\beta_1\}/[OAc] \times 10^{-8}$
0.2540	400.0	1.00	3.94	27.71
0.2545	328.6	1.22	4.78	27.69
0.2550	279.7	1.43	5.61	27.67
0.2555	229.7	1.74	6.82	27.66
0.2560	200.0	2.00	7.81	27.65
0.2565	175.2	2.28	8.90	27.64
0.2570	151.0	2.65	1.03	27.64

Fig. 3.6 Plots of $[\text{Ni(II)} - \text{NH}_4\text{OAc-OXAc}]$ (At constant 0.25M AcOH)
system for Amberlite IR-120

$(D_0/D-1)/[\text{OX}]$ vs $[\text{OX}]$



$(D_0/D-1)/[\text{OX}]^2 - \beta_1$ vs $[\text{OX}]$

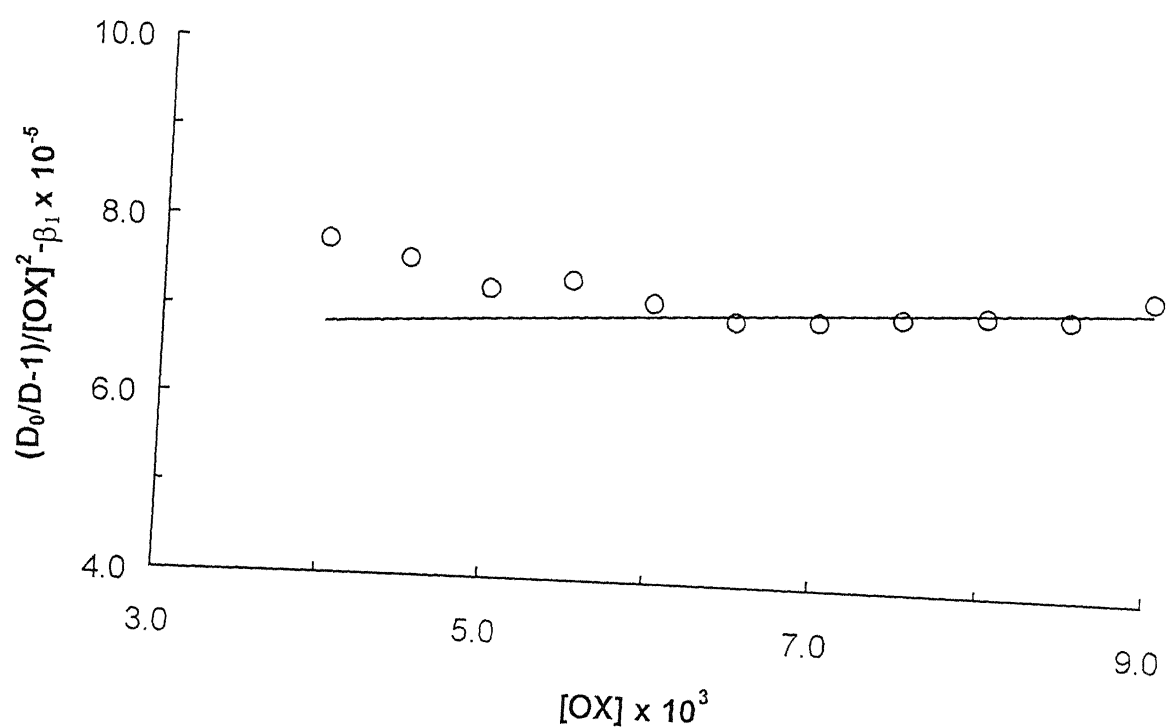


Fig. 3.7 Plots of $[M - NH_4OAc-OXAc]$ (At constant 0.25M AcOH) system for Amberlite IR-120

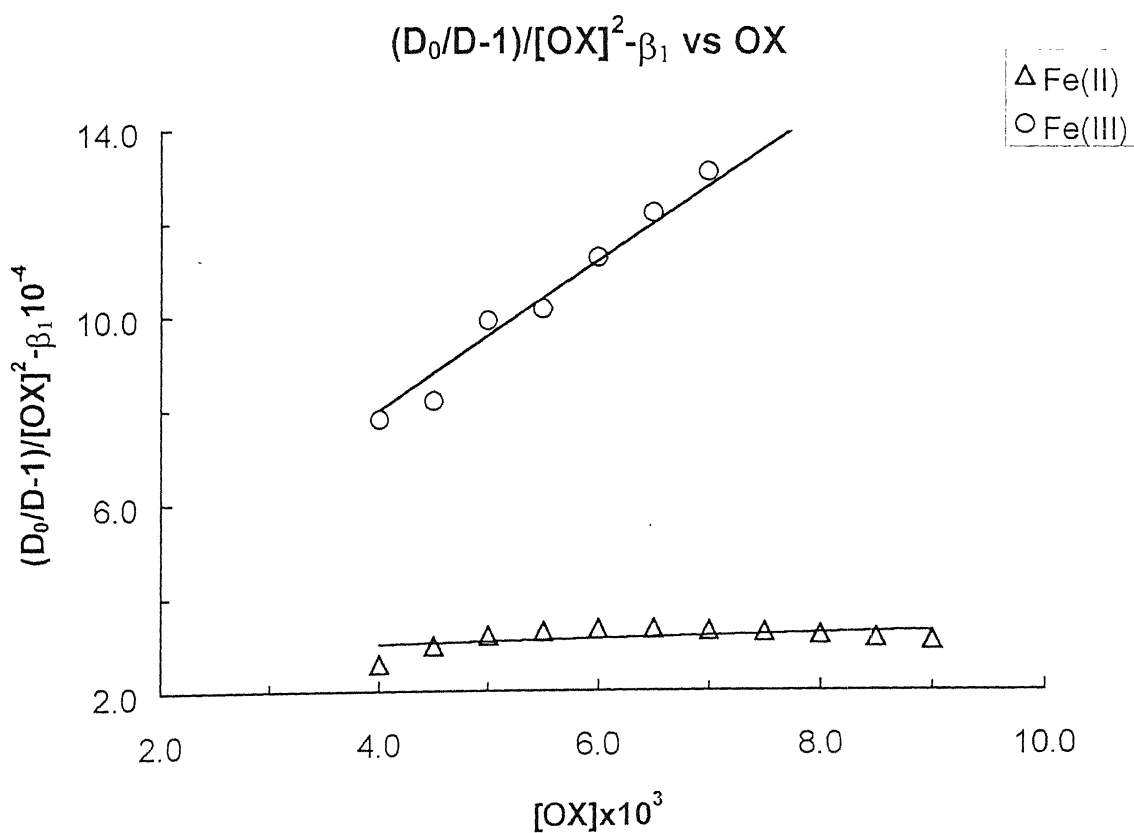
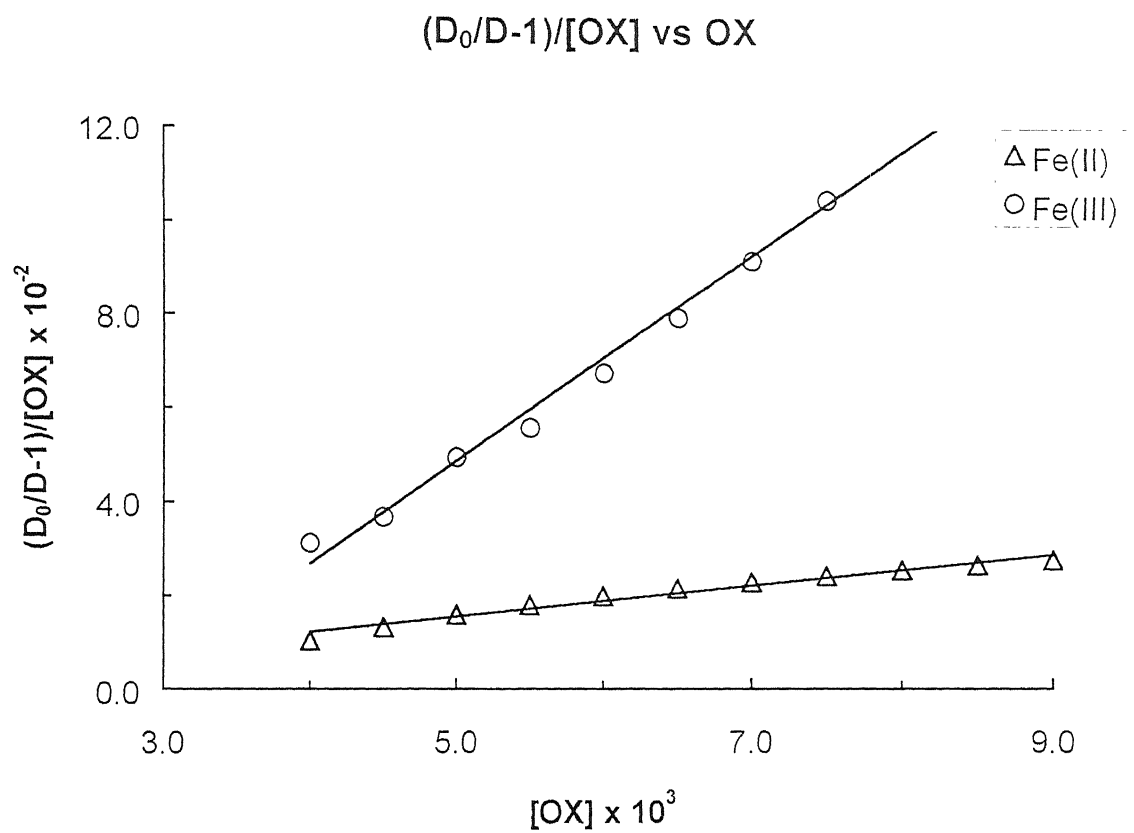


Fig. 3.8 Plots of $[M - NH_4OAc-OXAc]$ (At constant 0.25M AcOH) system for Amberlite IR-120

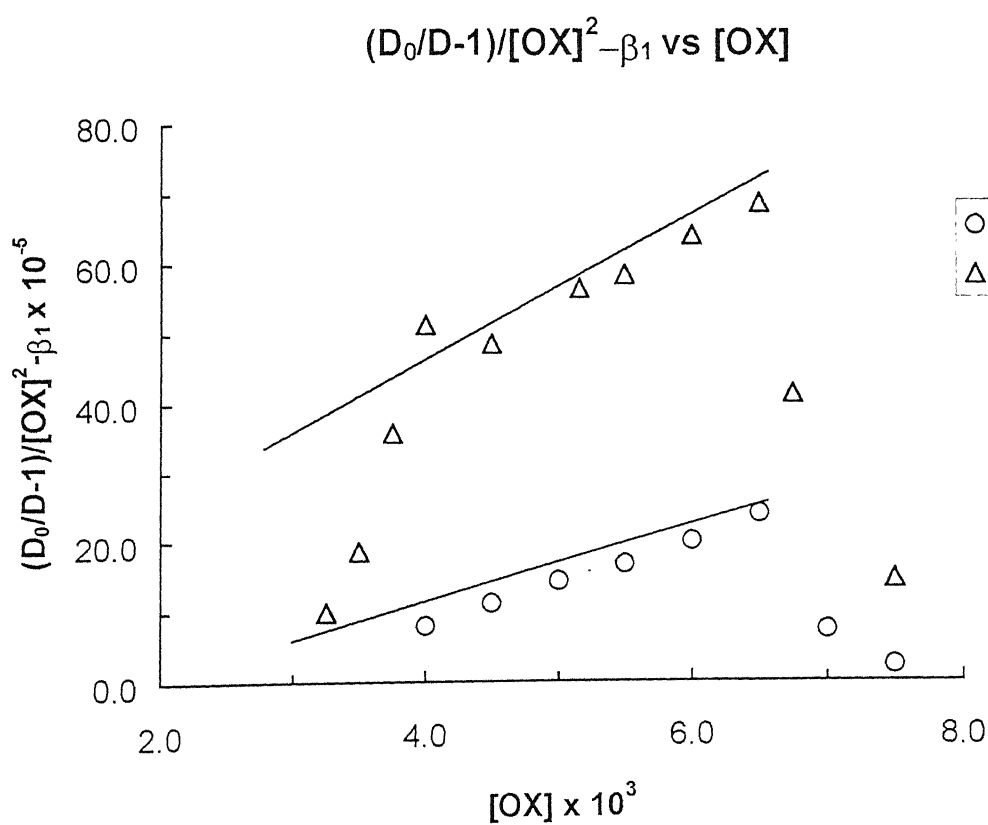
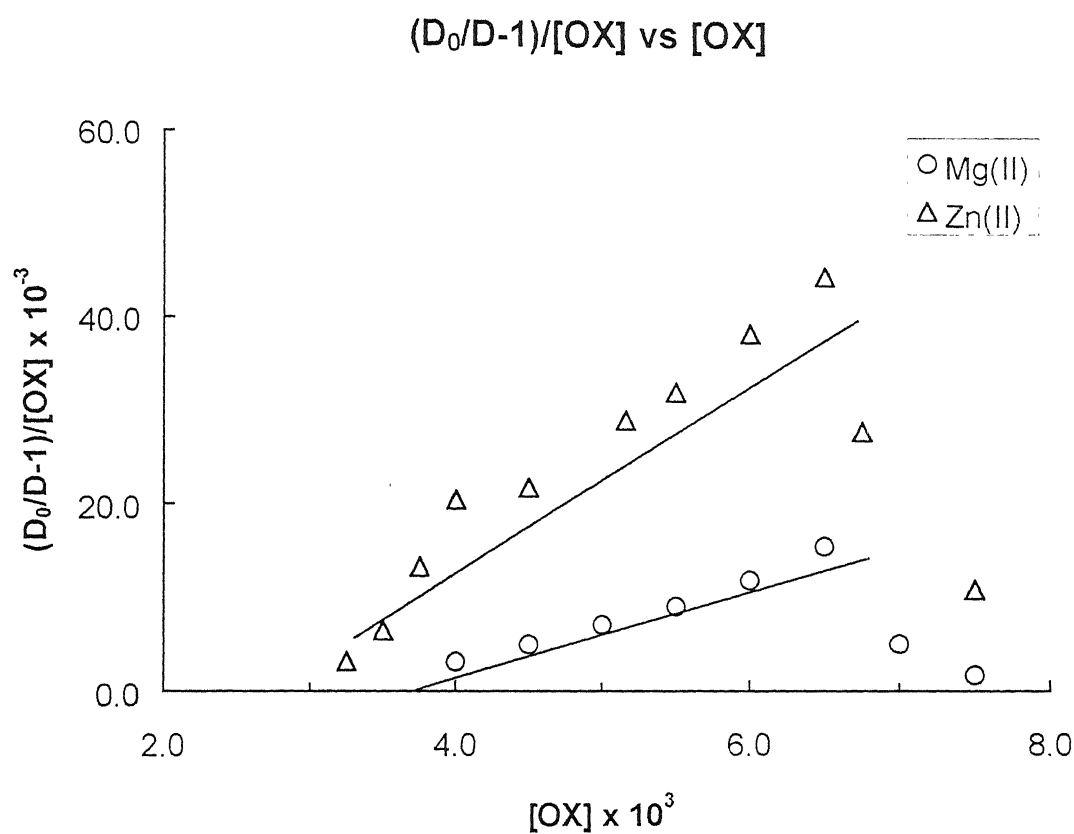
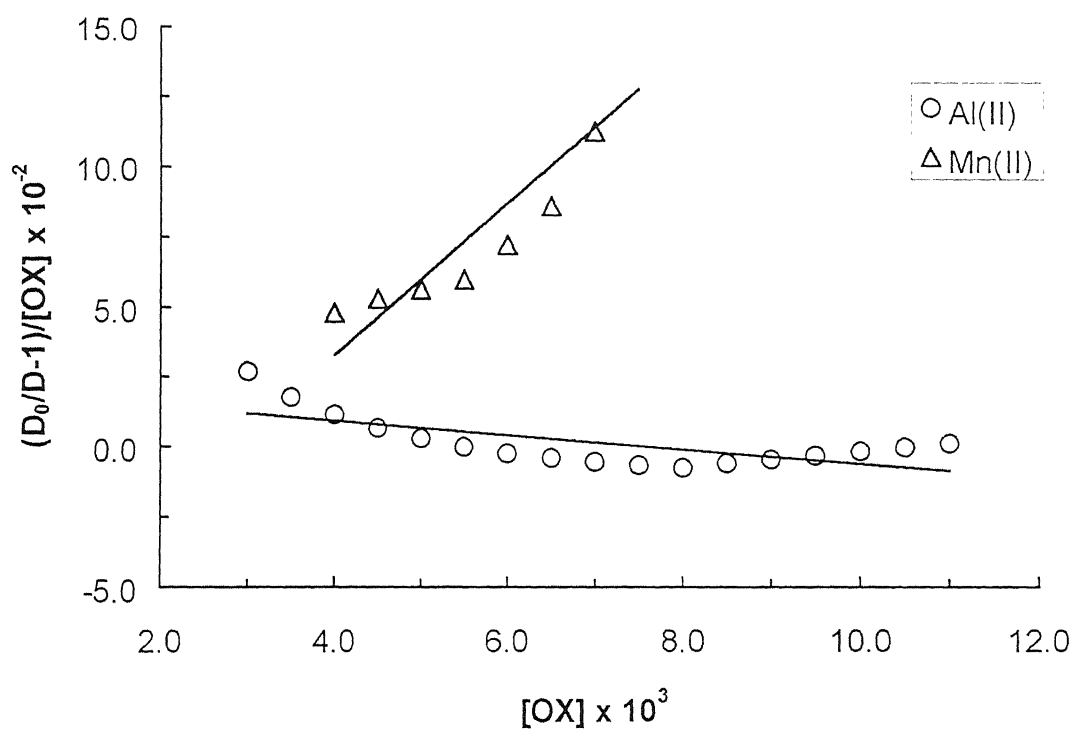
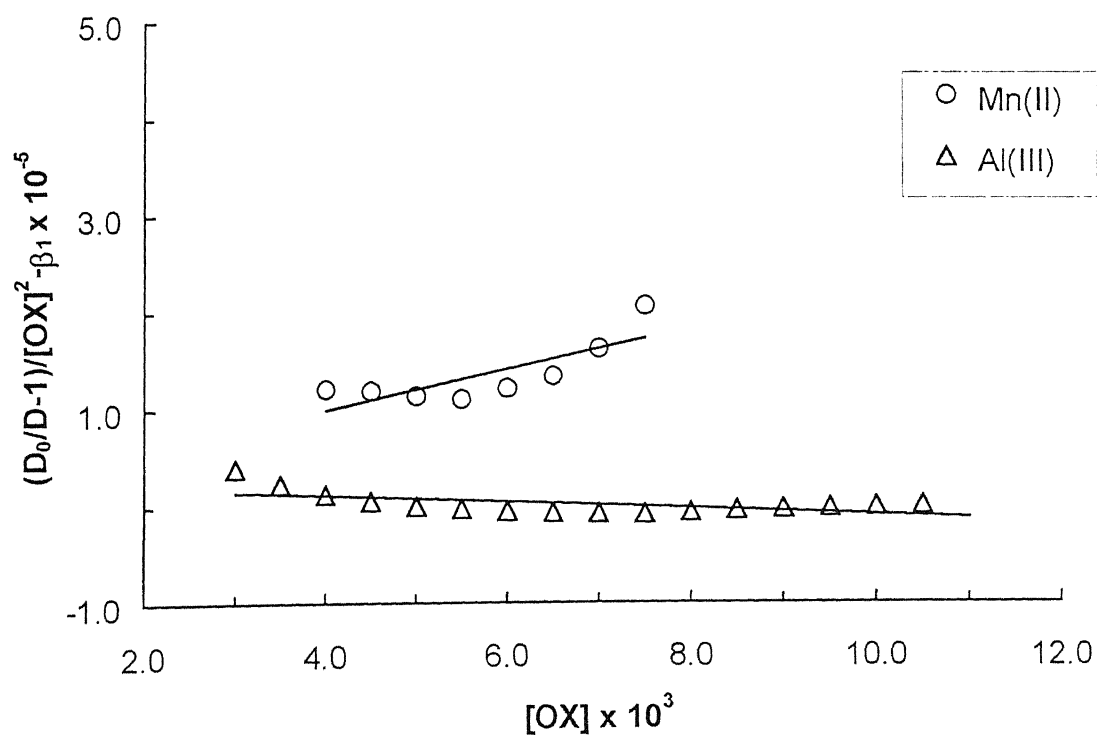


Fig. 3.9 Plots of $[M - NH_4OAc-OXAc]$ (At constant 0.25M AcOH) system for Amberlite IR-120

$(D_0/D-1)/[OX]$ vs OX



$(D_0/D-1)/[OX]^2 - \beta_1$ vs $[OX]$



0.2575	130.8	3.06	11.9	27.65
0.2580	114.3	3.50	13.6	27.66
0.2585	101.3	3.95	15.3	27.67
0.2590	87.5	4.57	17.7	27.71

Table- 3.19: Shubert's Function and Other Calculated Variables of Zn(II) in mixed NH₄OAc – OXAc media ([AcOH] = 0.25M) on Amberlite IR –120(NH₄⁺–form)

[OAc]M	D	$\{(D_0/D)-1\} \times 10^{-3}$	$(D_0/D-1)/[OAc] \times 10^{-3}$	$\{(D_0/D-1)/[OAc]\}-\beta_1/[OAc] \times 10^{-7}$
0.25325	2900.0	0.8	3.03	1.31
0.25350	1400.0	1.6	6.27	1.31
0.25375	650.0	3.4	13.5	1.31
0.25400	400.0	5.6	21.9	1.31
0.25450	310.9	7.2	28.1	1.30
0.25500	233.3	9.5	37.4	1.30
0.25550	177.7	12.5	49.0	1.30
0.25600	150.0	14.8	58.0	1.30
0.25650	114.2	19.5	76.0	1.30
0.25700	400.0	5.6	21.6	1.29

Table: 3.20: The calculation of the equilibrium formation constants of the studied metal ions have also been worked out with respect to complexation with acetate

Metal Ion	D ₀	log k ₁	logβ ₂	logβ ₃
Mg(II)	562866076	9.5	10.4	10.6
Mn(II)	7232	8.1	8.7	9.6
Fe(II)	66510752	4.3	5.1	5.4
Fe(III)	46367786	7.1	8.3	8.6
Ni(II)	37762816	7.9	8.4	9.3
Zn(II)	2198016	7.8	8.9	9.3
Al(III)	10403231	6.5	7.4	7.6

The values of the formation constant of oxalate determined by application of various approaches are not so different as well as are not so close to on comparing with the values reported in the literature. The deviations with some of the metal studied are high as compared to oxalato species log K values of literature. Like the values evaluated for oxalate which have been found a little higher than the reported literature values, here also the acetate log K values are found higher comparative to literature values. As no approach has still being developed to investigate the mixed

ligand system present calculation the related equilibrium formation constant have been determined ignoring either acetate or oxalate for approximate calculations of the oxalate formation constant or acetate formation constant of the metal ions in order to throw light and to explain the sorption tendencies and affinities of investigated metal ions in these media. It has been observed that in both the cases (either of oxalate or of acetate formation constants) the values obtained are higher showing that the acetate as well as oxalate are simultaneously coordinating with the metal ion, resulting to mixed ligand species and this mixed complexation is probably responsible for the higher formation constant values. The higher values of metal-acetate complex species showing that though complexation with the acetate is definitely responsible for increasing the complexing with the metal ion. Thus unique and unexplained behavior of the acetate medium is a landmark observation for the formation of species in such media. Their nature is much complicated, therefore, the formation tendencies of these complexes are worked out with respect to oxalate concentrations present in the equimolar mixture solution, and these may be comparable only to certain extent with the absolute values of the complexes.

Mixed complexation is also affected the sorption behaviour, may be in a different fashion and can not be compare with the single ligand complexation behaviour. Therefore, the peculiar sorption curves were obtained especially in cases of Mg (II), Zn (II), and Al (III).

It is proposed that the species as compound will be isolated and separated from the solution as well as resin (by deposition) phases for their characterization by other techniques as a future plan research work

ANION EXCHANGE STUDIES

Resin Capacity: - Accurately weighed quantity (1.0g, 2.0g, 3.0g, 4.0g, and 5.0g) of the anion exchanger (Amberlite IRA – 400 in Cl^- - form) was transferred in a column by making a survey with water. After several rinses with water, the chloride was effluent with ca.10% NaNO_3 solution until effluent was free from chloride. The effluent flow speed was kept ~1.0mL/minute. The chloride content in the aliquot of the effluent was determined by usual method (106). The capacity was found 2.654 meq/g of air-dried resin Table 3.21. The method recommended by Helfferich (106)

was also employed to evaluate the resin capacity and the results obtained by both the method showed good agreement. The moisture content was determined by the usual method and was found to be 23.05%.

Table - 3.21: Determination of Resin Capacity by column experiment Amberlite IRA-400 (Cl⁻ – form, 50-100 mesh,) Eluting Agent–10.0%NaNO₃

Amount of resin	Total Diluted Vol. Of H ⁺ Effluent	Total Vol. Of (M/20) AgNO ₃ used for 25 mL of Cl ⁻ Effluent (mL) (b)	Corresponds vol. Of AgNO ₃ Total Cl ⁻ Effluent Vol.(v) (mL)	Capacity =(bv/w) in milli equivalent of Cl ⁻ /g of Resin
1.0	100.0	13.19	52.76	2.640meq/g
2.0	100.0	26.37	105.48	2.648meq/g
3.0	250.0	15.81	158.1	2.650meq/g
4.0	250.0	21.60	216.0	2.642meq/g
5.0	250.0	26.37	263.7	2.650meq/g

DISTRIBUTION STUDIES

The distribution coefficient (D) values (Table 3.22) are determined in the similar way as described in cases of cation exchange study. Basically the D-values of these anion exchange processes differ to those of cation exchange studies due to distribution of anionic species instead cationic species. The corresponding loading values are summarised in Table 3.23. The plots of metal ion D-values Vs [OX] and %L Vs [OX] are given in Fig. 3.10 and 3.11 respectively.

Table-3.22: Values of Distribution Coefficient (D) of NH₄OAc – OXAc media (AcOH = 0.25M) of Amberlite IRA - 400 (Cl⁻ - form)

Concentration of [OX] x 10 ³	Distribution Coefficient of Metal Ion						
	Mg(II)	Al(II)*	Mn(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)**
4.00	25.0	53.9	76.5	7.3	8.3	25.0	25.0
4.25	33.9	50.0	82.5	7.8	10.9	27.5	28.5
4.50	42.8	46.4	88.5	8.3	13.5	30.4	32.1
4.75	54.7	42.8	94.45	8.8	16.3	33.0	37.1
5.00	66.6	39.5	100.0	9.4	19.2	35.7	42.8
5.25	80.0	36.3	106.2	10.1	22.3	39.6	49.5
5.50	93.5	33.6	112.7	10.7	25.5	43.5	56.2
5.75	121.7	30.4	126.3	11.1	29.0	46.7	61.2
6.00	150.0	27.9	140.0	11.5	32.6	50.0	66.6
6.25	195.0	25.0	147.1	12.1	36.5	53.9	77.0
6.50	240.0	22.5	154.2	12.8	40.5	57.9	87.5
6.75	118.9	20.0	193.7	13.1	45.0	62.2	38.8
7.00	66.6	17.65	233.3	13.5	49.5	66.6	25.0
7.25	39.5	15.3	280.9	13.8	54.4	71.5	P
7.50	25.0	17.65	328.5	14.5	59.4	76.5	P
7.75	P	20.0	328.5	15.1	65.2	82.0	P
8.00	P	22.5	328.5	15.8	71.0	87.5	P
8.25	P	25.0	328.5	16.4	77.65	93.7	P
8.50	P	27.9	328.5	17.1	84.3	100.0	P
8.75	P	30.4	328.5	17.6	100	107.6	P
9.00	P	33.6	328.5	18.1	100	115.2	p

P = precipitate

* = reading taken from 3.0 X 10⁻³ up to 13 X 10⁻³M of [OX] concentration see in discussion

** = reading taken from 3.25 X 10⁻³M of [OX] concentration it shows in discussion

Fig. 3.10 Distribution Coefficient (D) vs [OX]
For Amberlite IRA-400

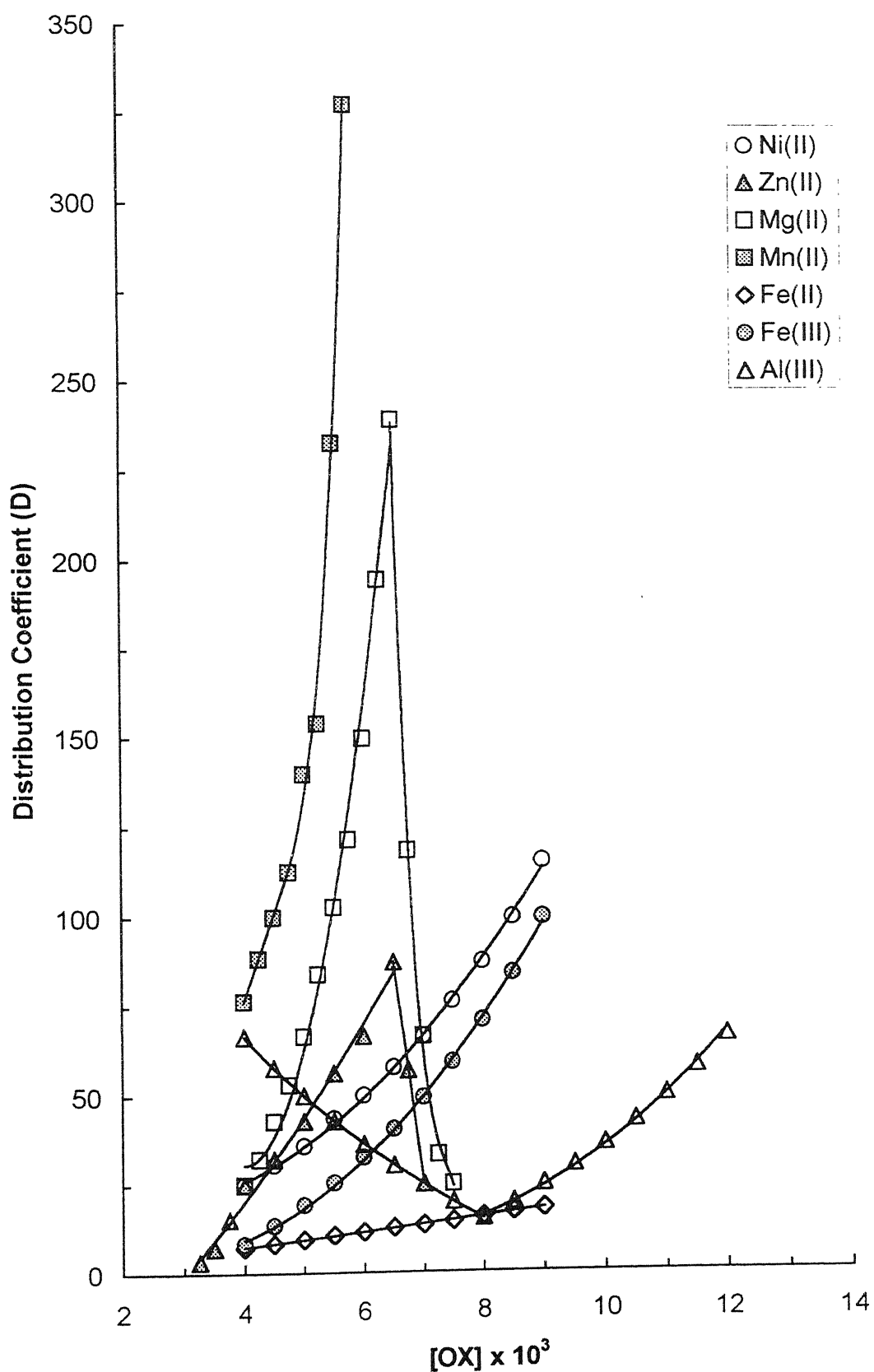


Fig. 3.11 Percentage Loading (L%) vs [OX]
For Amberlite IRA-400

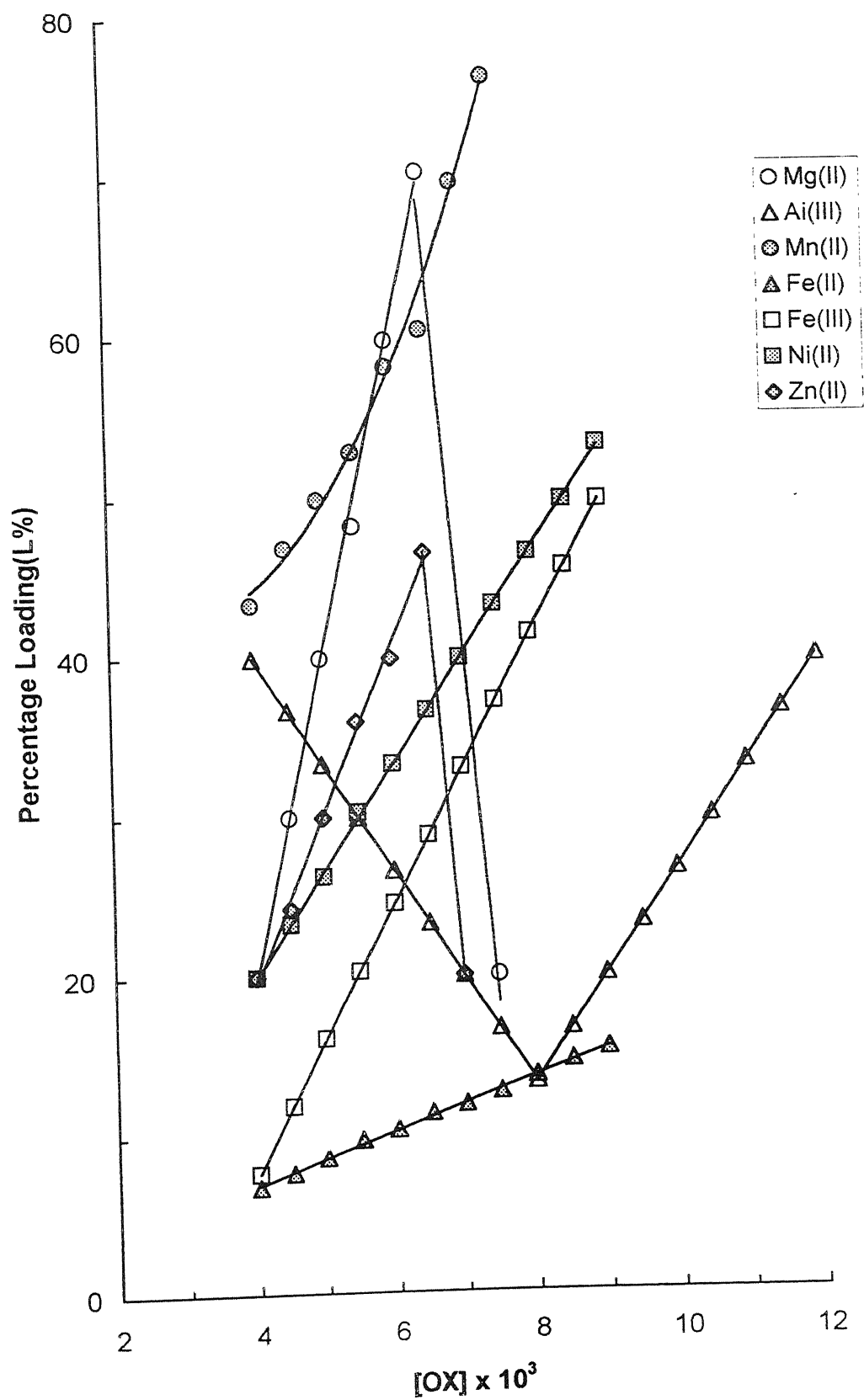


Table-3.23: Values of Percentage Loading (L%) of NH₄OAc – OXAc media
(AcOH = 0.25M) of Amberlite IR- 400 (Cl⁻ - form)

Concentration of [OX] x 10 ³	Percentage Loading (L%) Metal Ion						
	Mg(II)	Al(II)*	Mn(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)**
4.00	20.0	35.0	43.3	6.8	7.7	20.0	20.0
4.25	25.3	33.3	45.2	7.2	9.8	21.6	22.2
4.50	30.0	31.7	46.9	7.7	11.9	23.3	24.3
4.75	35.4	30.0	48.6	8.1	14.0	24.8	27.1
5.00	40.0	28.3	50.0	8.6	16.1	26.3	30.0
5.25	44.4	26.6	51.5	9.2	18.2	28.4	33.1
5.50	48.3	25.1	53.0	9.7	20.3	30.3	36.0
5.75	54.9	23.3	55.8	10.0	22.5	31.8	38.0
6.00	60.0	21.8	58.3	10.3	24.6	33.3	40.0
6.25	66.1	20.0	59.5	10.8	26.7	35.0	43.5
6.50	70.6	18.4	60.7	11.3	28.8	36.7	46.7
6.75	54.3	16.7	66.0	11.6	31.0	38.3	28.0
7.00	40.0	15.0	70.0	11.9	33.1	40.0	20.0
7.25	28.3	13.3	73.7	12.1	35.2	41.7	P
7.50	20.0	15.0	76.7	12.7	37.3	43.3	P
7.75	P	16.7	76.7	13.1	39.5	45.1	P
8.00	P	18.4	76.7	13.6	41.5	46.7	P
8.25	P	20.0	76.7	14.1	43.7	48.4	P
8.50	P	21.8	76.7	14.6	45.7	50.0	P
8.75	P	23.3	76.7	15.0	50.0	51.8	P
9.00	P	25.125	76.7	15.3	50.0	53.5	P

P = precipitate

* = reading taken from 3.0 X 10⁻³ to 13 X 10⁻³ M of [OX] concentration see in discussion

** = reading taken from 3.25 X 10⁻³ M of [OX] concentration it shows in discussion

RESULT AND DISCUSSION

The anion exchange behaviour of the individual metal ions indicate the sorption trends are not following a well defined increasing or decreasing pattern in selected concentration range of NH₄OAc-OXAc mixture solution. On the basis of experimentally established observations, the investigated metal ions are not showing a close sorption trend. Metal ions Ca(II), Cd(II), Cu(II), Co(II), La(III), Pb(II), Th(II), which were tried in these media could not be studied due to either insolubility of their

oxalates probably formed in chosen mixed solutions of NH_4OAc - OXAc - AcOH or due to formation of their hydrolytic species causing precipitation

Metal ions Mn (II) , Fe (II and III) , and Ni (II) had shown a gradual increase of D-values indicating involvement of these metal ions in the complexation activities leading to gradual more uptake by the resin. The D-plot of Fe(II) is a straight line while that of Mn(II) , Fe(II) and Ni(II) are curved which is clearly showing that the displacement of coordination water is not same rather it differs metal to metal and consequently the complexation equilibrium is affected and this may be responsible for obtaining curves of similar nature for these metal ions (Ni(II) , Fe(III) and Mn(II)) plots. The displacement of coordination water in Fe(II) is so that it is resulted to a straight line. The other important factors, which are definitely playing significant role in these observed deviation of the sorption tendencies (of the studied metal ions), may be linked with the activities of the other various species present in these systems. All ionic species are not only affecting the metal ion charge and its concentration impact, but they are solubilizing the whole medium and overall affecting the ion exchange distribution equilibrium of these metal ions. Similarly the various unavoidable thermodynamic considerations are simultaneously contributing to the metal complexation equilibria as well as respective ion exchange equilibria putting the gross effect on the metal distribution between the solid resin and aqueous solution phases.

Mg (II) shows a very unique sorption behaviour, i.e., its sorption not following the usual trend instead the lower sorption is observed at 4.00×10^{-3} equimolar $\text{OXAc-NH}_4\text{OAc}$ mixture (constant 0.25M AcOH) solution with a D-values=25.0. A gradual increase observed at 6.25×10^{-3} equimolar mixture solution and then again the D-values are decreasing up to 7.50×10^{-3} equimolar solution with same D-value=25.0. It has also been observed that at lower concentration, i.e., 3.75×10^{-3} equimolar mixture solution, and at higher concentration, i.e., 7.75×10^{-3} equimolar mixture solution, experiments could not be performed due to precipitation indicating the dominance of species having neutral charge.

The gradual increase from lowest D-value 25 to highest 240.0 can not be simply explained by taken into account the usual complexation considerations. The medium contains cations H^+ and NH_4^+ apart the metal ion Mg^{2+} and the anions,

$\text{C}_2\text{O}_4^{2-}$, CH_3COO^- and a little SO_4^{2-} (corresponding to Mg^{2+}). The oxalate and the acetate may be participating in the complexation or interaction with the magnesium as well as with the cations NH_4^+ and H^+ , which are also taking part in the competitive sorption with the magnesium. The sorption equilibrium is shifted that first the uptake of magnesium is increasing but after reaching to a highest value it starts decreasing showing definitely change in the nature of sorbable species or the competitive sorption tendencies of H^+ and NH_4^+ now no more so effective may be due to the buffering effect of the medium. Therefore their sorptions are increased as well as the buffering and solvalization of the medium also appears some way operating so that the complexation of Mg with oxalate and the acetate is also increased only a certain limited concentration range of the mixed equimolar mixture solution. But at $6.75 \times 10^{-3}\text{M}$ concentration the decrease in D-value started which may be caused by the disproportionation of the anionic species to free Mg^{2+} or the cationic magnesium species leading to this gradual decrease in D-values of magnesium.

Zn (II) also showing to some extent the similar type of behaviour like Mg (II). But it may not be exactly like Mg (II) and only at the last three concentrations before the precipitation starts, a decrease has been observed in the D values of Zn(II). Like magnesium same equilibria of complexation, competitive sorption and buffering as well as solvalization are responsible for this trend of sorption of Zn(II) in the investigated range of equimolar oxalic acid and ammonium acetate mixture solutions. Zinc is a last member of the first transition series (may not be considered by definition a transition element) and definitely possesses a different or relatively deviated complexing nature than Mg, and the observed little deviation in its sorption may be contributed by this inherent transitory factor.

The sorption trend of Al (III) is just reverse of the Mg(II) which is also a very unique and abnormal behaviour observed in these investigated media,

The complexation tendencies of Al (III) with oxalate and/or acetate are relatively operating in such a fashion that the gross anionic species formation is gradually decreasing and the D-values are showing gradual decrease till $8.0 \times 10^{-3}\text{M}$ equimolar mixture solution. But beyond this or higher concentration the decreasing trend has changed to an increasing pattern, which has definitely been resulted due to strong complexation and formation of more and more anionic species at higher

concentration ranges. This may also be contributed by the gradual suppression of the hydrolysis or other phenomenon responsible for the disproportion of the anionic species between the 3.00×10^{-3} to 8.0×10^{-3} concentration ranges.

The various steps for the treatment of anion exchange distribution data of metal OXAc-NH₄OAc system at constant 0.25M AcOH have also been worked out by considering the various mathematical approximations to be applied for different equilibria dominating in solution at a particular range of concentration of the selected media. The stability constants have been evaluated using the treatments of the modified form of Froneous Method (chapter-2). The complexation equilibria in solution may be given as described for the cation exchange systems. The overall gross metal ion exchange distribution for a metal-ligand system having species ML₃ may be given as,

$$D = \frac{([ML_2] + [ML_3])}{([ML] + [ML_2] + [ML_3])} \quad \text{--- (9)}$$

Taking into account the distribution of individual species according to equation (6) from chapter 2 then

$$D = \frac{(\lambda_2 \beta_2 [L]^2 + \lambda_3 \beta_3 [L]^3)}{(1 + k_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3)} \quad \text{--- (10)}$$

where, λ_2 and λ_3 indicates the distribution coefficient of ML₂ and ML₃ species, respectively

$$D = \frac{(\lambda_2 \beta_2 [L]^2 + \lambda_3 \beta_3 [L]^3)}{(1 + F)} \quad \text{--- (11) Where } F = k_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3$$

on rearranging,

$$D(1 + F) = \lambda_2 \beta_2 [L]^2 + \lambda_3 \beta_3 [L]^3 \quad \text{--- (12)}$$

or,

$$\frac{D + DF}{\lambda_3 [L]^3} = \frac{\lambda_2 \beta_2 [L]^2}{\lambda_3 [L]^3} + \beta_3 \quad \text{--- (13)}$$

or,

$$\frac{D}{\lambda_3 [L]^3} = \frac{\lambda_2 \beta_2}{\lambda_3 [L]} + \beta_3 - \frac{F.D}{\lambda_3 [L]^3} \quad \text{--- (14)}$$

or,

$$\frac{D}{[L]^2} = \lambda_2 \beta_2 + \lambda_3 \beta_3 [L] - \frac{F.D}{[L]^2} \quad \text{--- (15)}$$

and from equations (14) and (15) on extrapolating the curves $D/\lambda_3[L]^3$ vs $1/[L]$ and $D/[L]^2$ vs $[L]$ to zero $[L]$ concentration β_3 and $\lambda_2\beta_2/\lambda_3$ are obtained as the limiting values or the intercepts for ML_2 species .

On substituting the values of β_3 and $\lambda_2\beta_2$ in the equation (15) and rearranging, then

$$\left(\frac{1}{[L]^2} - \frac{\beta_2\lambda_2}{D} \right) = \left(\frac{\beta_3\lambda_3[L]}{D} - \beta_2 \right) - \frac{1}{[L]^2} (K_1[L] + \beta_3[L]) \text{ --- (16)}$$

the plot $(1/[L]^2 - \beta_2\lambda_2/D)$ (or denoted as ϕ in the tables) Vs $[L]/D$ was extrapolated to zero $[L]$ concentration and β_2 was evaluated as limiting value of the intercept. (Fig. 3.12, 3.13, 3.14, 3.15, 3.16, 3.17, 3.18). The various experimental parameters and the calculated quantities as per mathematical equations are given in Table 3.24, 3.25, 3.26, 3.27, 3.28, 3.29, 3.30.

Table- 3.24: Ni(II)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

(OX)x 10 ⁻³	D	D/(OX) ² x10 ⁻⁶	D/λ ₃ [OX] ³ x 10 ⁻⁶	1/(OX) x10 ⁻²	1/(OX) ² - β ₂ λ ₂ /D x10 ⁻³	(OX)/D x10 ⁵
4.00	25.00	1.56	3.4	2.5	14.1	16.0
4.50	30.43	1.50	2.9	2.2	9.6	14.8
5.00	35.74	1.43	2.5	2.0	6.1	14.0
5.50	43.54	1.44	2.3	1.8	5.2	12.6
6.00	50.00	1.39	2.0	1.7	3.6	12.0
6.50	57.89	1.37	1.8	1.5	2.7	11.2
7.00	66.66	1.36	1.7	1.4	2.2	10.5
7.50	76.47	1.36	1.6	1.3	1.9	9.8
8.00	87.60	1.37	1.5	1.3	1.8	9.1
8.50	100.0	1.38	1.4	1.2	1.7	8.5
9.00	115.8	1.43	1.4	1.1	1.9	7.8

Table–3.25: Zn(II)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

(OX)x 10 ⁻³	D	D/(OX) ² x10 ⁻⁵	D/λ ₃ (OX) ³ x10 ⁻⁶	1/[OX] x10 ⁻²	1/(OX) ² - β ₂ λ ₂ /D x10 ⁻³	(OX)/D x10 ⁵
3.25	3.40	3.22	1.13	3.08	-119.51	95.59
3.50	7.10	5.80	1.89	2.86	-20.94	49.30
3.75	15.3	10.88	3.32	2.67	23.51	24.51
4.00	25.0	15.63	4.46	2.50	33.37	16.00
4.50	32.1	15.85	4.03	2.22	26.70	14.02

5.00	42.8	17.12	3.91	2.00	22.98	11.68
5.50	56.2	18.58	3.86	1.82	20.10	9.79
6.00	66.6	18.50	3.52	1.67	16.84	9.01
6.50	87.5	20.71	3.64	1.54	15.35	7.43
7.00	57.0	12.51	2.12	1.48	9.17	11.84
7.25	25.0	5.10	0.83	1.43	-8.72	28.00

Table–3.26: Mg(II)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

$(OX) \times 10^3$	D	$D/(OX)^2 \times 10^{-6}$	$D/\lambda_3(OX)^3 \times 10^{-6}$	$1/(OX) \times 10^{-2}$	$1/(OX)^2 - \beta_2\lambda_2/D \times 10^{-5}$	$(OX)/D \times 10^5$
4.00	25.00	1.6	1.63	250	2.6	16.0
4.50	42.80	2.1	1.96	222	1.7	10.5
5.00	66.60	2.7	2.22	200	1.1	7.5
5.50	102.8	3.4	2.57	182	0.8	5.4
6.00	150.0	4.2	2.89	167	0.6	4.0
6.50	240.0	5.7	3.64	154	0.4	2.7
7.00	66.60	1.4	0.81	143	1.0	10.5
7.50	25.00	0.4	0.25	133	2.2	30.0

Table–3.27: Mn(II)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

$OX \times 10^3$	D	$D/(OX)^2 \times 10^{-6}$	$D/\lambda_3(OX)^3 \times 10^{-6}$	$1/(OX) \times 10^{-2}$	$1/(OX)^2 - \beta_2\lambda_2/D \times 10^{-3}$	$(OX)/D \times 10^5$
4.00	76.50	4.78	3.64	2.50	20.22	5.23
4.50	88.50	4.37	2.96	2.22	12.84	5.08
5.00	100.0	4.00	2.44	2.00	7.66	5.00
5.50	112.7	3.73	2.07	1.82	4.36	4.88
6.00	140.0	3.89	1.98	1.67	4.68	4.29
6.50	154.2	3.65	1.71	1.54	2.70	4.22
7.00	233.3	4.76	2.07	1.43	6.55	3.00
7.50	328.5	5.84	2.37	1.33	7.93	2.28

Table–3.28: Fe(II)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

$(OX) \times 10^3$	D	$D/(OX)^2 \times 10^{-5}$	$D/\lambda_3(OX)^3 \times 10^{-6}$	$1/(OX) \times 10^{-2}$	$1/(OX)^2 - \beta_2\lambda_2/D \times 10^{-4}$	$(OX)/D \times 10^4$
4.00	7.30	4.56	6.30	2.50	-2.07	5.48
4.50	8.30	4.10	5.03	2.22	-2.38	5.42
5.00	9.40	3.76	4.15	2.00	-2.46	5.32
5.50	10.7	3.54	3.55	1.82	-2.37	5.14

6.00	11.5	3.19	2.94	1.67	-2.50	5.22
6.50	12.8	3.03	2.58	1.54	-2.38	5.08
7.00	13.5	2.76	2.17	1.43	-2.46	5.19
7.50	14.5	2.58	1.90	1.33	-2.41	5.17
8.00	15.8	2.47	1.70	1.25	-2.28	5.06
8.50	17.1	2.37	1.54	1.18	-2.17	4.97
9.00	18.1	2.23	1.37	1.11	-2.12	4.97

Table–3.29: Fe(III)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

$(\text{OX}) \times 10^3$	D	$D/(\text{OX})^2 \times 10^{-5}$	$D/\lambda_3(\text{OX})^3 \times 10^{-6}$	$1/(\text{OX}) \times 10^{-2}$	$1/(\text{OX})^2 - \beta_2 \lambda_2 / D \times 10^{-4}$	$(\text{OX})/D \times 10^4$
4.00	8.30	5.19	1.30	2.50	5.20	4.82
4.50	13.5	6.67	1.48	2.22	4.29	3.33
5.00	19.2	7.68	1.54	2.00	3.54	2.60
5.50	25.5	8.43	1.53	1.82	2.96	2.16
6.00	32.6	9.06	1.51	1.67	2.51	1.84
6.50	40.5	9.59	1.47	1.54	2.15	1.60
7.00	49.5	10.10	1.44	1.43	1.86	1.41
7.50	59.4	10.56	1.41	1.33	1.63	1.26
8.00	71.0	11.09	1.39	1.25	1.44	1.13
8.50	84.3	11.67	1.37	1.18	1.28	1.01
9.00	100.0	12.35	1.37	1.11	1.15	0.90

Table–3.30: Al(III)–NH₄OAc–OXAc (at AcOH=0.25M) Amberlite IRA-400 system treatment of the data by the modified method of Fronaeus

$(\text{OX}) \times 10^3$	D	$D/(\text{OX})^2 \times 10^{-6}$	$D/\lambda_3(\text{OX})^3 \times 10^{-7}$	$1/(\text{OX}) \times 10^{-2}$	$1/(\text{OX})^2 - \beta_2 \lambda_2 / D \times 10^{-4}$	$(\text{OX})/D \times 10^4$
3.00	87.5	5.47	11.39	2.50	6.00	0.46
3.50	75.4	3.72	6.90	2.22	4.65	0.60
4.00	66.6	2.66	4.44	2.00	3.67	0.75
4.50	57.9	1.91	2.90	1.82	2.93	0.95
5.00	50.0	1.39	1.93	1.67	2.34	1.20
5.50	42.8	1.01	1.30	1.54	1.86	1.52
6.00	36.3	0.74	0.88	1.43	1.44	1.93
6.50	30.4	0.54	0.60	1.33	1.06	2.47
7.00	25.0	0.39	0.41	1.25	0.69	3.20
7.50	20.0	0.28	0.27	1.18	0.29	4.25
8.00	15.3	0.19	0.17	1.11	-0.19	5.88
8.50	20.0	0.22	0.19	1.05	0.02	4.75
9.00	25.0	0.25	0.21	1.00	0.13	4.00

Fig. 3.12 Plots of [Mg(II) - NH₄OAc-OXAc](At constant 0.25M AcOH) system for Amberlite IRA-400

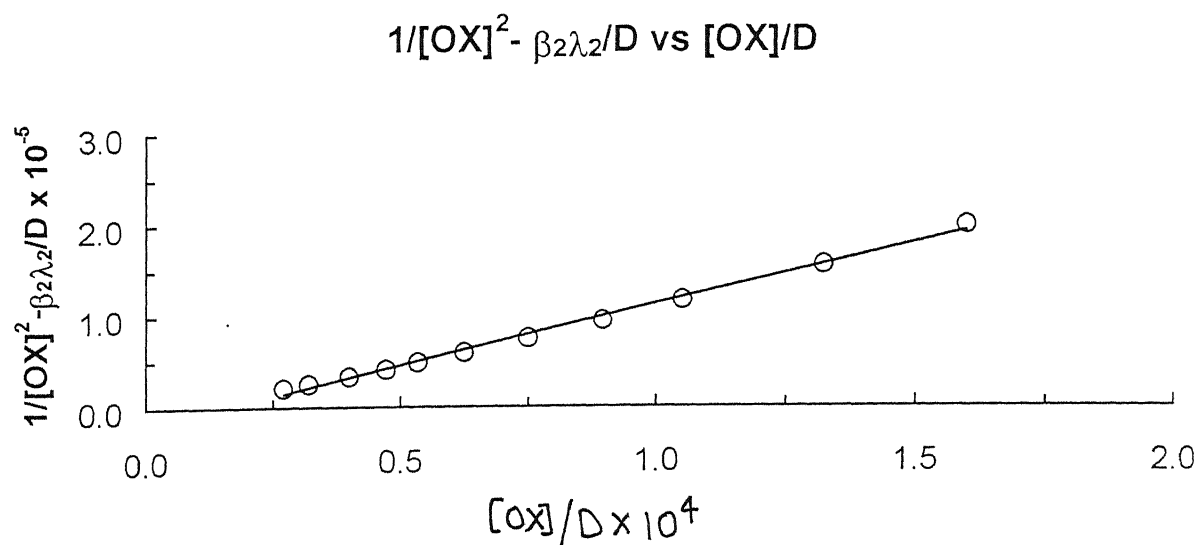
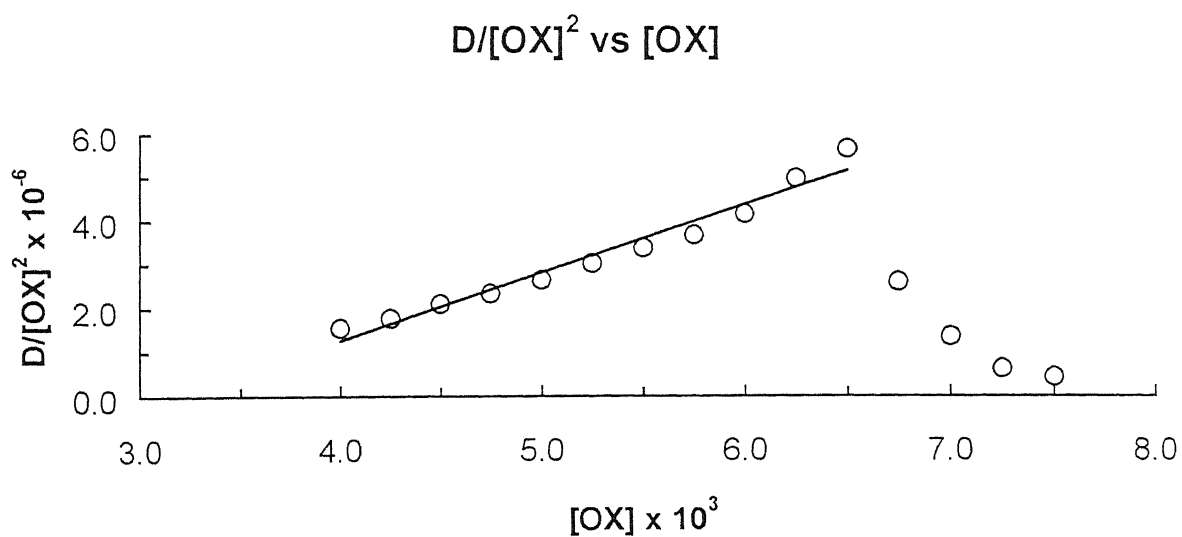
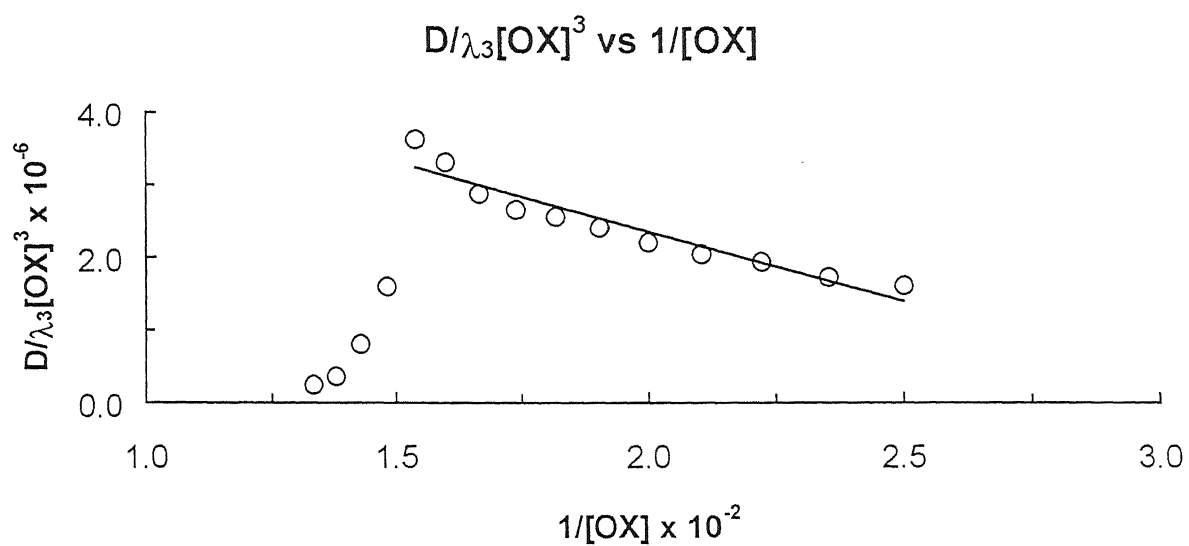


Fig. 3.13 Plots of [Mn(II) - NH₄OAc-OXAc](At constant 0.25M AcOH)
system for Amberlite IRA-400

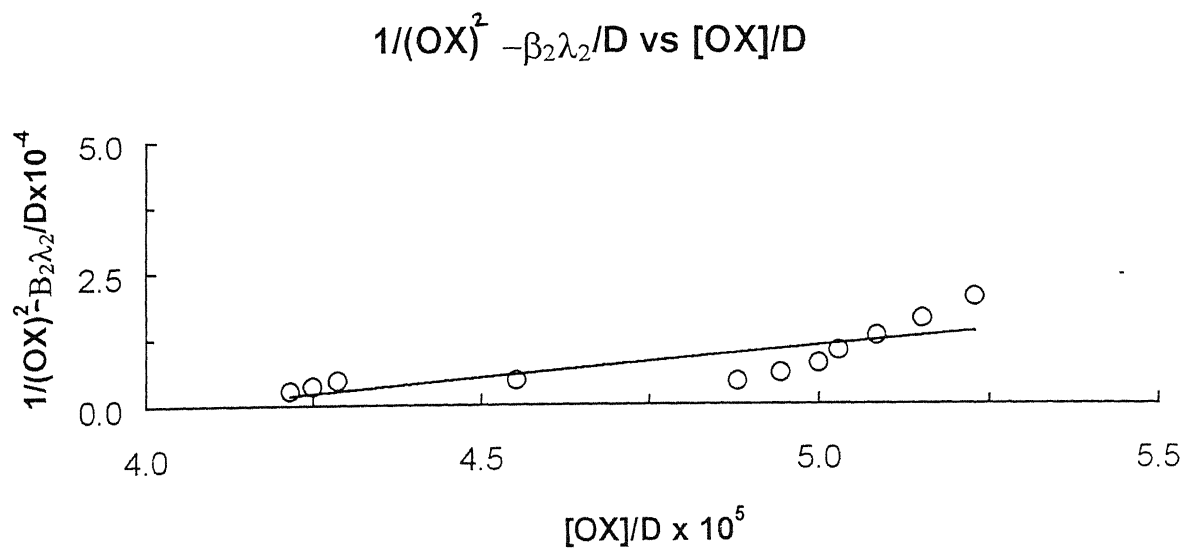
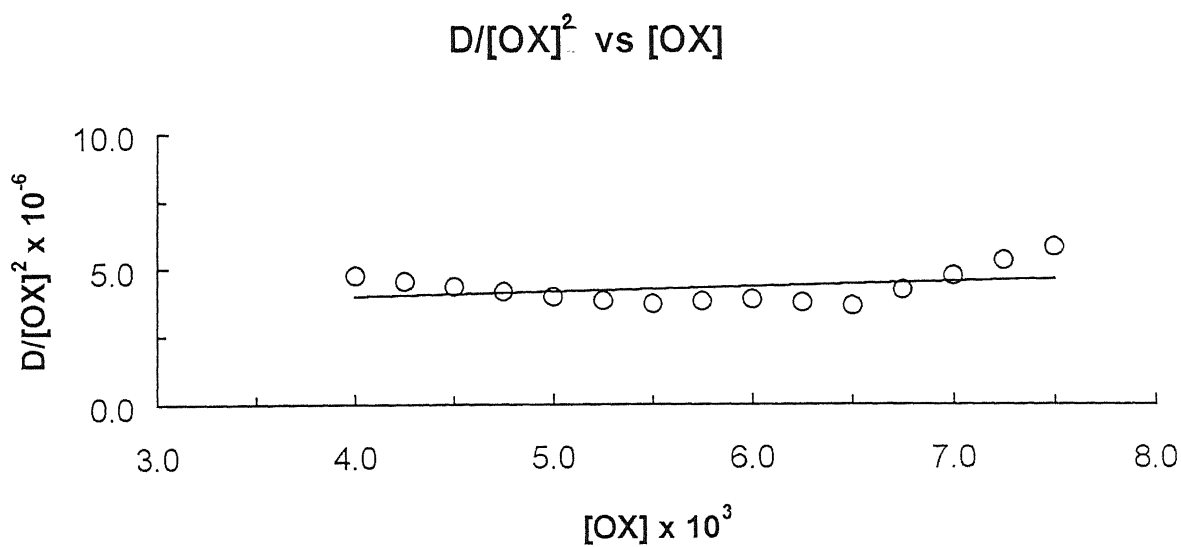
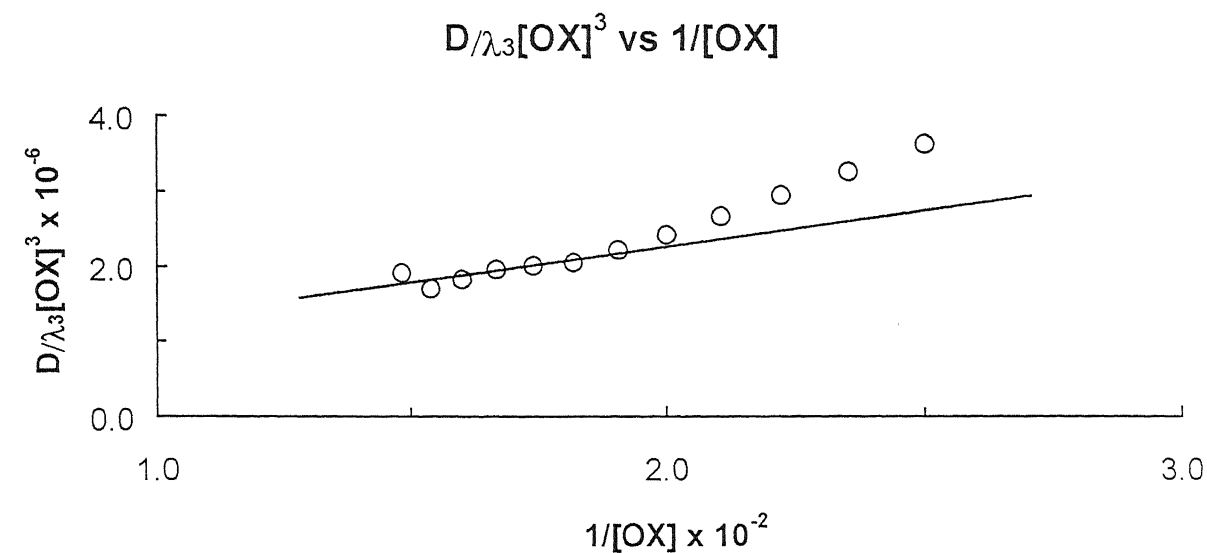
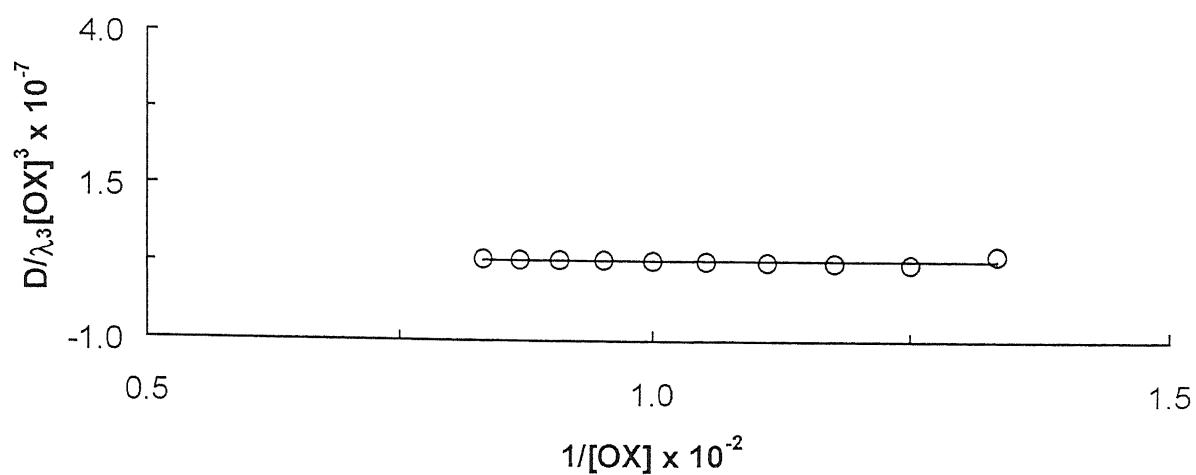
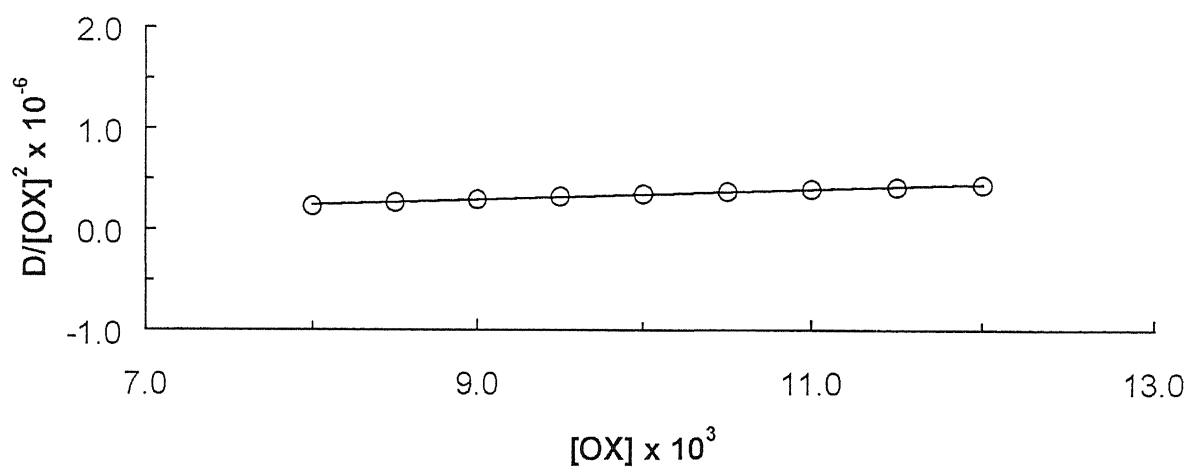


Fig. 3.14 Plots of [Al(III) - NH₄OAc-OXAc](At constant 0.25M AcOH) system for Amberlite IRA-400

$D/\lambda_3[\text{OX}]^3$ vs $1/[\text{OX}]$



$D/[\text{OX}]^2$ vs $[\text{OX}]$



$1/(\text{OX})^2 - \beta_2\lambda_2/D$ vs $[\text{OX}]/D$

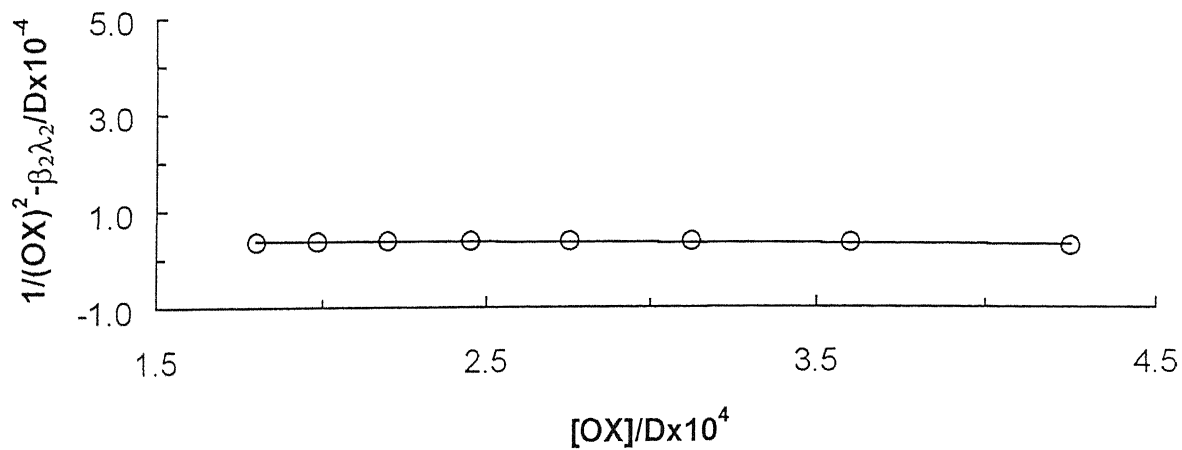
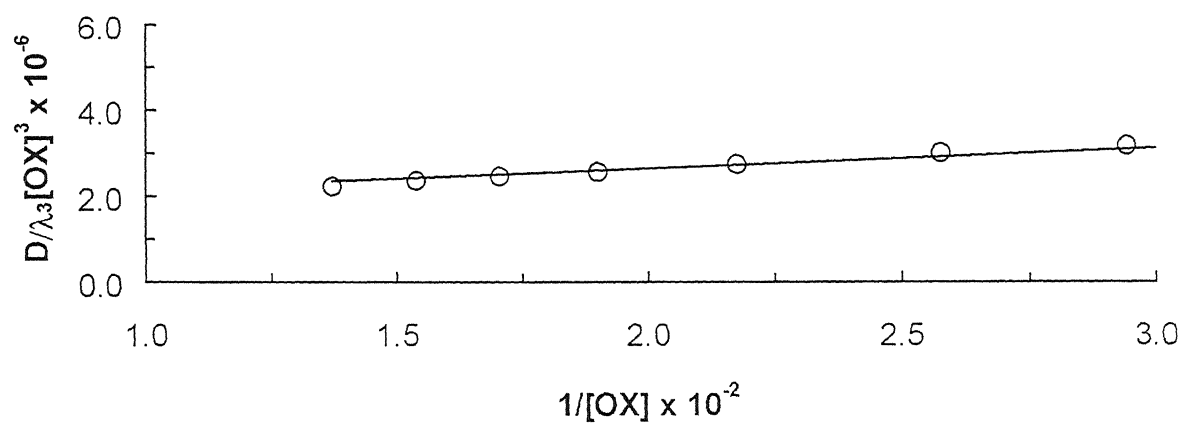
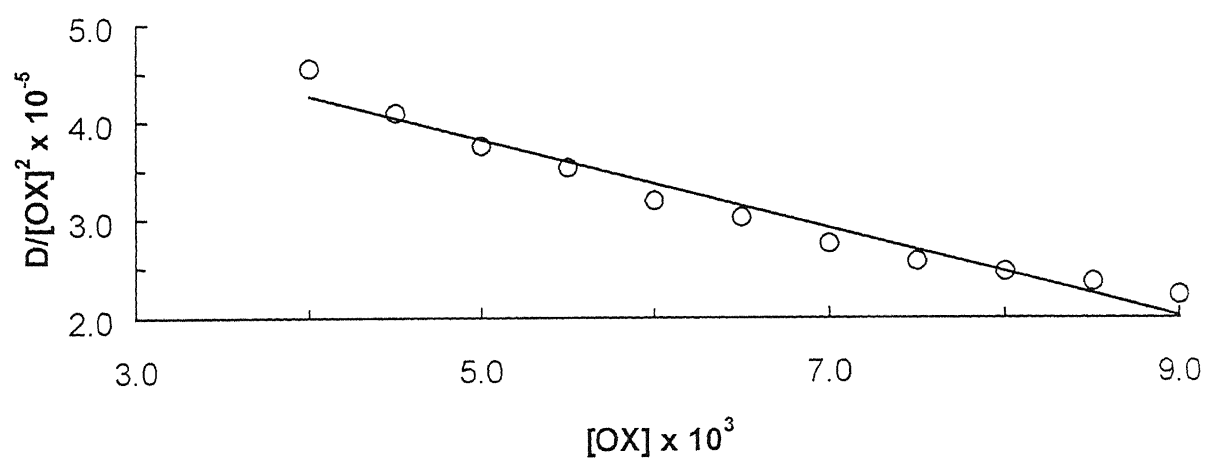


Fig. 3.15 Plots of [Fe(II) - NH₄OAc-OXAc](At constant 0.25M AcOH)
system for Amberlite IRA-400

$D/\lambda_3[\text{OX}]^3$ vs $1/[\text{OX}]$



$D/[\text{OX}]^2$ vs $[\text{OX}]$



$1/(\text{OX})^2 - \beta_2\lambda_2/D$ vs $[\text{OX}]/D$

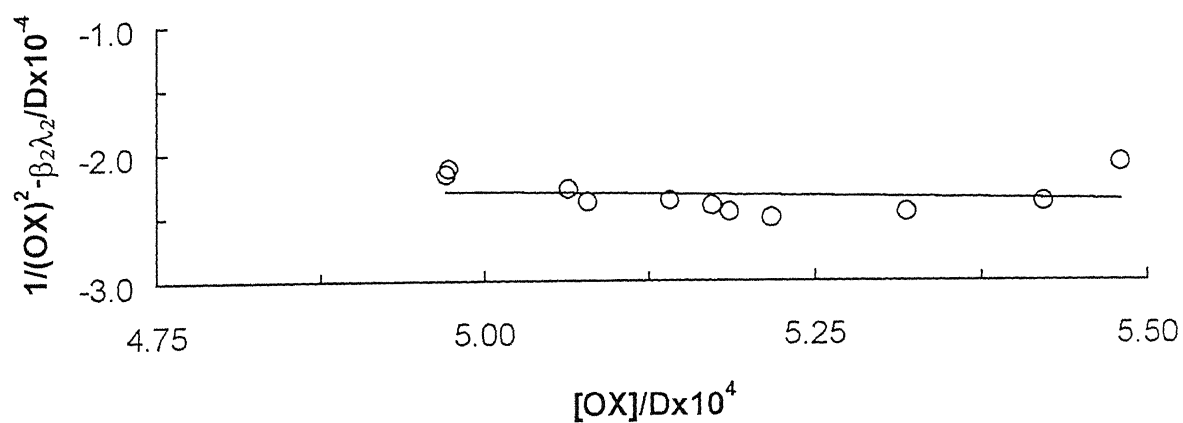
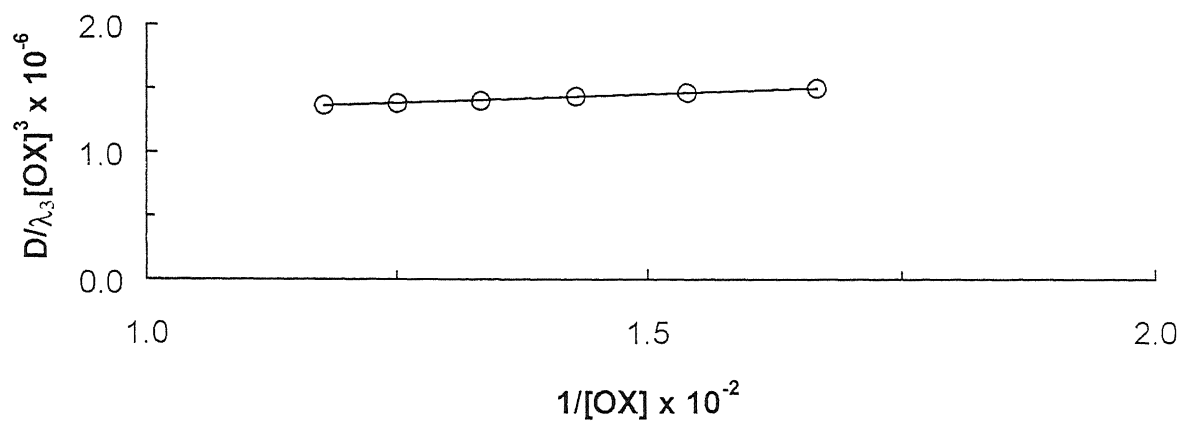
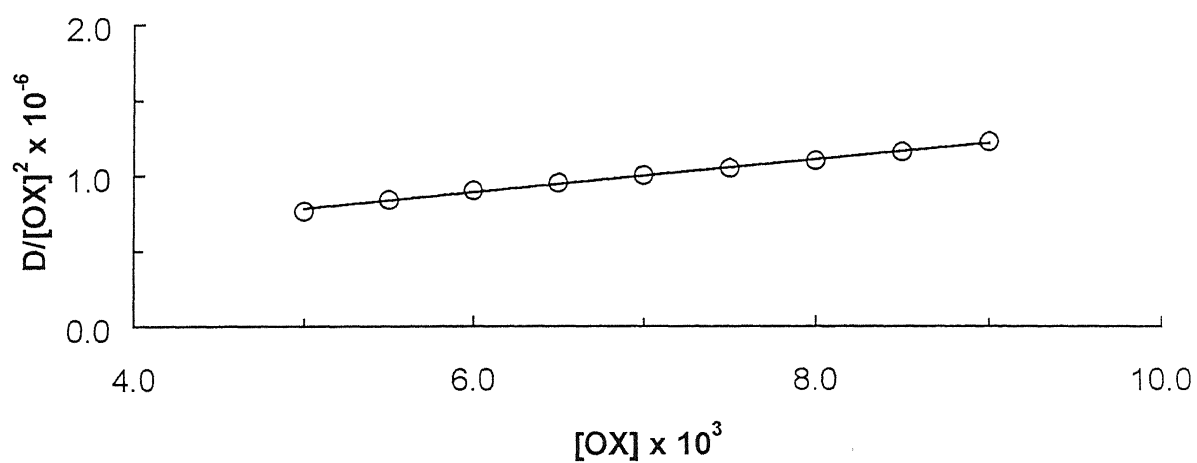


Fig. 3.16 Plots of [Fe(III) - NH₄OAc-OXAc](At constant 0.25M AcOH) system for Amberlite IRA-400

$D/\lambda_3[\text{OX}]^3$ vs $1/[\text{OX}]$



$D/[\text{OX}]^2$ vs $[\text{OX}]$



$1/(\text{OX})^2 - \beta_2\lambda_2/D$ vs $[\text{OX}]/D$

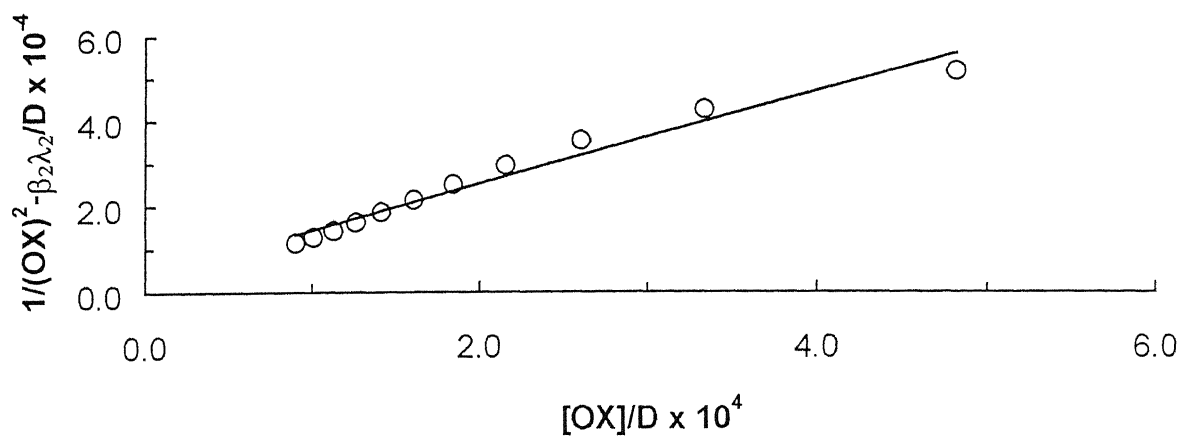


Fig. 3.17 Plots of [Ni(II) - NH₄OAc-OXAc](At constant 0.25M AcOH)
system for Amberlite IRA-400

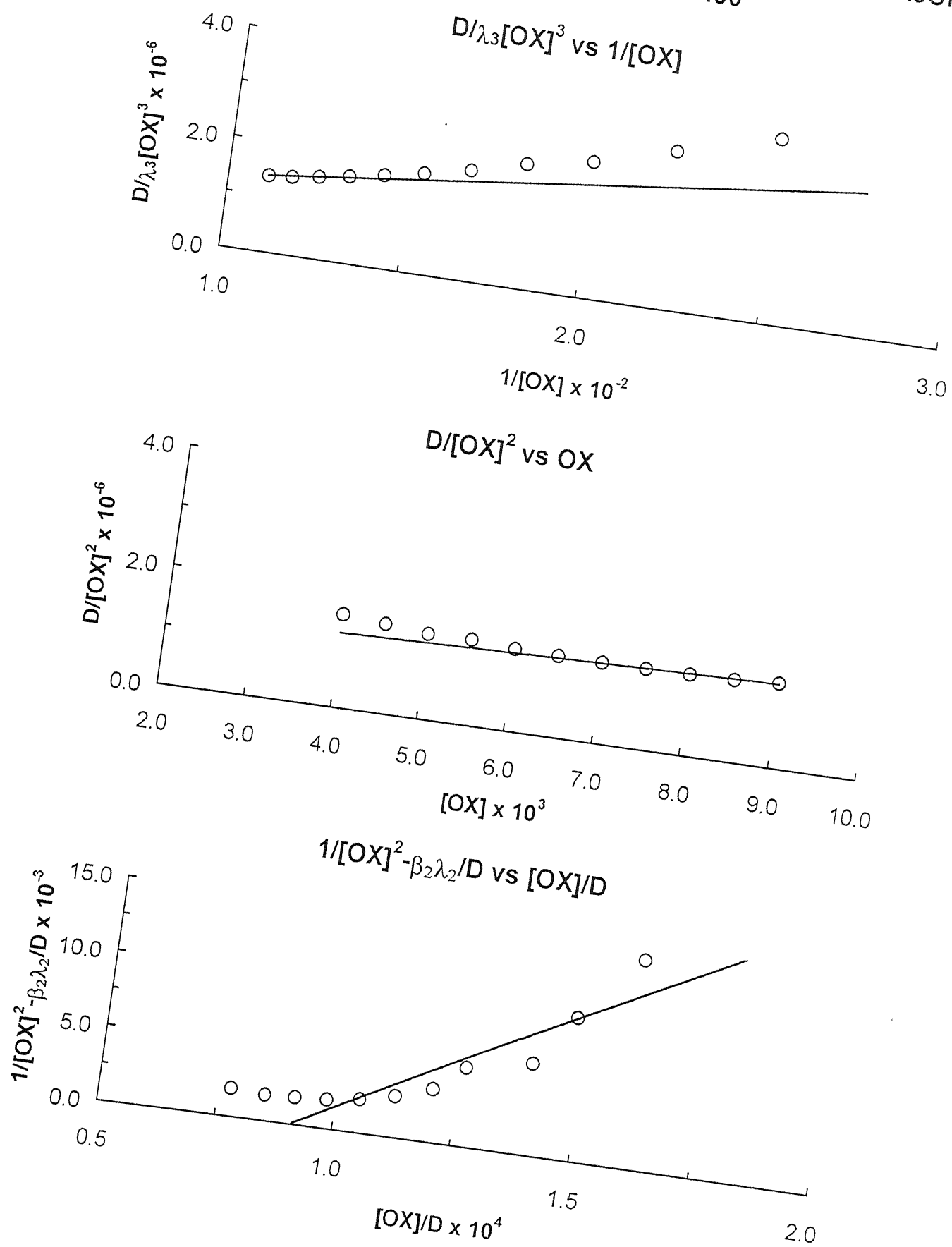
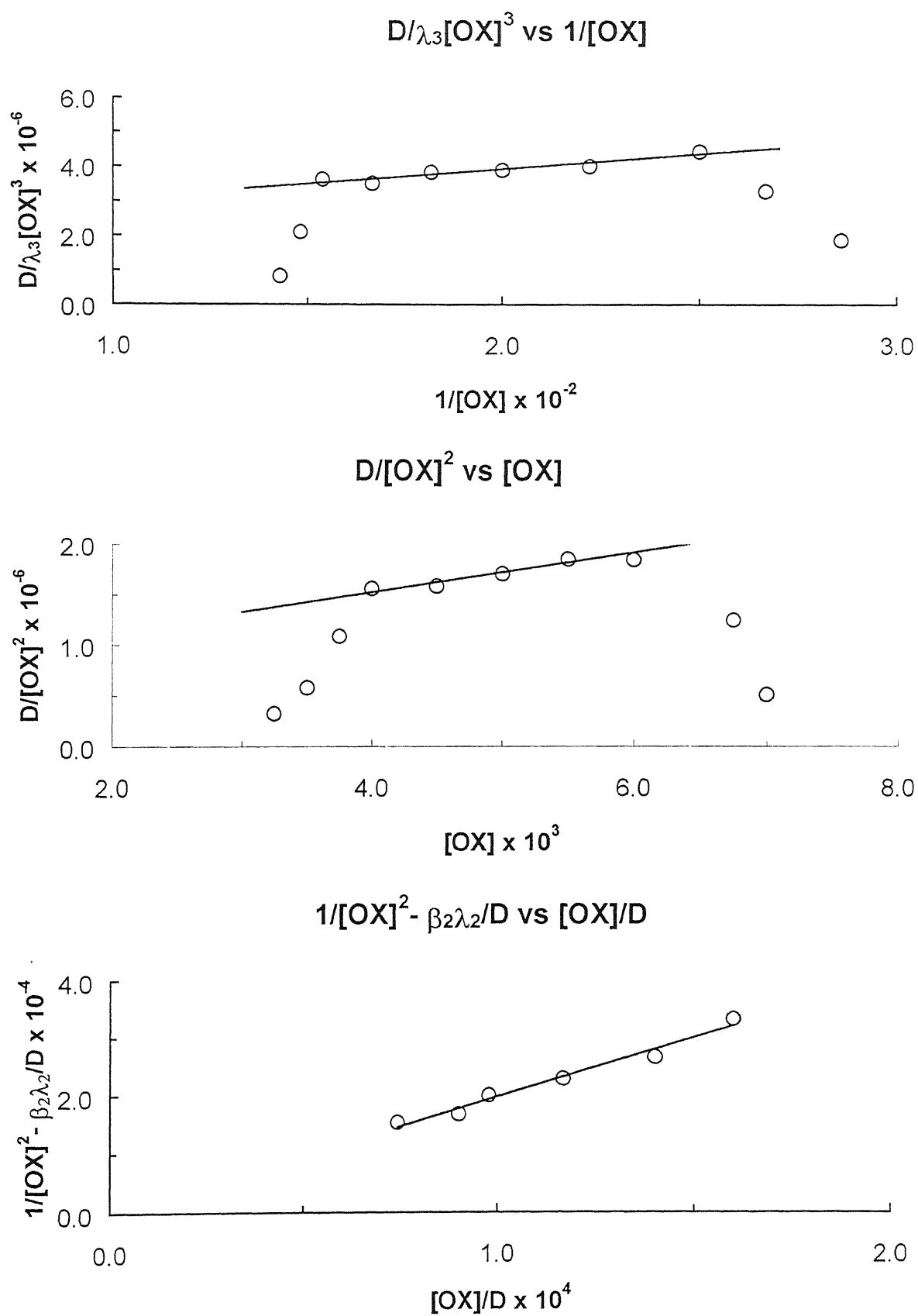


Fig. 3.18 Plots of [Zn(II) - NH₄OAc-OXAc](At constant 0.25M AcOH) system for Ambe rlite IRA-400



9.50	30.4	0.28	0.22	0.95	0.19	3.45
10.0	36.3	0.30	0.23	0.91	0.23	3.03
10.5	42.8	0.32	0.23	0.87	0.25	2.69
11.0	50.0	0.35	0.24	0.83	0.26	2.40
11.5	57.9	0.37	0.25	0.80	0.26	2.16
12.0	66.6	0.39	0.25	0.77	0.26	1.95
12.5	75.4	0.41	0.26	0.74	0.26	1.79
13.0	87.5	0.45	0.27	0.71	0.26	1.60

The values of the formation constant (Table 3.31,3.32) worked out by anion exchange method are a little low cation exchange method. Thus may be contributed due to a basic difference in the nature and structure of anion and cation exchangers, i.e., they are carrying different exchangeable groups and hence the nature of exchangeable sites can not be exactly comparable. Also, the available space in the resin phase for the incoming species may not be same. We know that the cationic species are always smaller than the anionic species, therefore, exchange equilibria of cation exchange and anion exchange have a major breakthrough at these size behavioral aspects. In comparison to cation exchange process the anion exchange sorption is always found less and this limitation could not be worked out completely in any of the existing ion exchange approach of evaluating the equilibrium constant.

Table-3.31: Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal Ion	Experimental value λ_3	Calculated value λ_3	λ_2	β_3	β_2	Experimental value $\lambda_3\beta_3$	Calculated value $\lambda_3\beta_3$	$\lambda_2\beta_2$
Mg(II)	240	259	1093	6516606	4563	527332080	1563985494	4989669
Mn(II)	328	336	601	575947	5378	116956272	188910778	3234093
Fe(II)	18.1	17.3	36	2724876	16645	49320256	45090020	607498
Fe(III)	100	101	64	1114250	3527	139914800	111425033	225806
Ni(II)	116	142	58	517470	15152	59923026	32710628	884642
Zn(II)	87.5	83.4	1100	2274498	662	192256488	199018587	728243
Al(III)	66.6	214	83	243000	2627	198564970	16183819	218241

Table-3.32: Log Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal ion	Experimental λ_3 value	Calculated λ_3 value	$\log \lambda_3$	$\log \beta_3$	$\log \beta_2$	$\log \lambda_2 \beta_2$	$\log \lambda_3 \beta_3$
Ni(II)	2.38	2.41	2.1	5.7	4.2	5.9	7.8
Zn(II)	2.52	2.53	1.9	6.4	2.8	5.9	8.3
Mg(II)	1.26	1.24	2.4	6.8	3.7	6.7	9.2
Mn(II)	2.00	2.00	2.5	5.8	3.7	6.5	8.3
Fe(II)	2.06	2.15	1.3	6.4	4.2	5.8	7.7
Fe(III)	1.94	1.92	2.0	6.1	3.5	4.9	8.1
Al(III)	1.82	2.33	1.8	5.4	3.4	5.3	7.2

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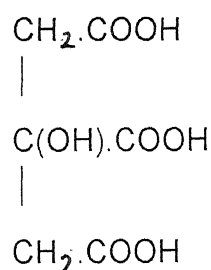
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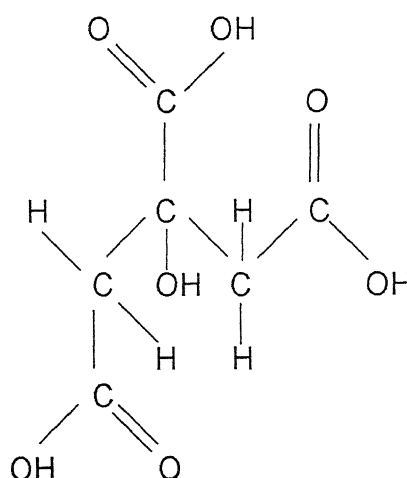
CHAPTER – 4

CATION AND ANION EXCHANGE STUDY OF METAL IONS IN AQUEOUS $(\text{NH}_4)_3\text{Cit}(\text{OH})$ MEDIA

Citric acid is an important compound and is being used in a number of ways. The potential application is as a starting material for obtaining other important compounds. It has a variety of application in the area of biotechnology and food technology (28). It is a hydroxy tricarboxylic acid, and occurs in the free state in many fruits (3) and as a metabolic product of many microorganism. Its molecule possesses a 5- member carbon-chain with three carboxylic acid groups and a hydroxy group. It is found in the unripe fruits of citraceae family plants and therefore the names are β -hydroxy-tricarballic acid(3), 2-hydroxy-1,2,3-propane-tricarboxylic acid / 2-hydroxypropane 1,2,3-tricarboxylic acid and 3-carboxy-3-hydroxy pentane-1,5-dioic acid (19) . The conventional formula and chemical structure of citric acid are (7)



Conventional formula



Normal Structural Formula

The aliphatic –OH group of citric acid does not dissociate releasing the proton (H^+), therefore, for simplicity it is written as $\text{H}_3\text{Cit(OH)}$ in this chapter, the various protonation and proton dissociation constant values reported in the literature according the following schemes are:

Protonation constants*	Protonation constants**	Dissociation constant***
At $I = 0$ (25°)	At $I = 1$ (25°)	At $I = 0$ (25°)
$\log K_{1(\text{H})} = 6.396$	$\log K_{1(\text{H})} = 5.0$	$-\log K_{3(\text{H})} = 3.08$ (7.4×10^{-4})
$\log K_{2(\text{H})} = 4.761$	$\log K_{2(\text{H})} = 3.70$	$-\log K_{2(\text{H})} = 4.74$ (1.8×10^{-5})
$\log K_{3(\text{H})} = 3.128$	$\log K_{3(\text{H})} = 2.25$	$-\log K_{1(\text{H})} = 5.40$ (4.0×10^{-7})

*= This values reported from ref.(17)

**= This values reported from ref.(12)

***= This values reported from ref.(1)

The ammonium ion (NH_4^+) plays a vary peculiar buffering activity in aqueous solution which has been observed in a series of various ammonium salts especially NH_4OAc in different studies, therefore, ammonium citrate $(\text{NH}_4)_3\text{Cit}(\text{OH})$ (7) was selected for these investigations. It has solubility of 100g/100g of water, and its 5% solution has the $\text{pH}=4.5 - 5.5$ (7). The one unit (in pH) variation again indicates its anomalous nature and the buffering behaviour, which may also be contributed due to the interactions with the solvent water having especial structural impact by H-bonding. The structure of water may not remain the same and changes by the presence of various species present in it. The overall such interactions affecting the structure of water may be causing the observed deviations in the pH values of such aqueous solutions. This further affects the dissociation or association interactions of the species quantitatively. It forms the mono-, di-, tri-ester derivatives with ammonia and ammonium salts, $\text{NH}_4\text{Cit}(\text{OH})\text{H}_2$, $(\text{NH}_4)_2\text{Cit}(\text{OH})\text{H}$, and $(\text{NH}_4)_3\text{Cit}(\text{OH})$ are produced depending upon the amount of the ammonia used.

The citric acid is being used for the manufacture of a large number of commercial products including drugs, and one of such compound is 1-phenyl,3-methyl pyrazolone an intermediate compound to be used for obtaining antipyrine and certain azo-dyes (6) . It is also used in the manufacture of edible synthetic ester resins (8).It has also been used extensively for a large number of ion exchange studies and many important separations have been reported which were successfully achieved in citric acid media. One of the very important separation is exemplified the isolation of plutonium and uranium for the production of atomic bombs(14), as well as high degree separation of rare earth elements providing their relatively salts in the pure forms.

Citric acid is also a biologically important molecule (11). Commonly it is used in the manufacture of citrates(3), flavoring extracts, confectionary, soft drinks, effervescent salts, as a silvering agent and as an ink gradient in engravings, in dyeing and calico printings(14), and in mediums. Now day's citric acid is obtained as a fermentation product

(19), which is an incomplete degradation of sugars in the absence of oxygen (anaerobic respiration).

Citric acid ($\text{H}_3\text{Cit}(\text{OH})$) is a promising complexing agent having three carboxylic acid groups and a hydroxy group. A number of metal complexes of citric acid were synthesized and characterized by Nguyen (25). These complexes are soluble in H_2O and exhibit various colours on artificial granites. Another study was carried out by Tsaramyrsi (30) to observe behaviour of citrate complex with Vanadium (30) which are inter conversant in aqueous solution. The protonated constants of citric acid were studied by Ghandour (12). He also studied the mixed legend complexes of Cd, Mg, Sr and Ca with citrate and pyruvate by pH-metric method at $\text{pH} = 0.5, 1.5, 2.0$, and considered the citrate as a primary ligand and pruvate as a secondary ligand and established the 1:1 complexes of these metals with citrate ligand. Polarographic method was used to investigate Cu(II)-citrate system (9). Fe (III)-citrate system has also been investigated (31,6,26) using different methods.

Apart the common mineral acids and a number of organic acids such as formic acid , oxalic acid complexing type tartaric, citric etc. have been found suitable separating media in a large number of metal ions. The simple ionic salts were also used as their aqueous solutions a good number of separations were achieved of non hydrolyzing metallic species but in case of transition metals and hydrolyzing cationic species the mixed acid solutions of these salts were used. It has been observed in our laboratories that the buffer media have some very typical and unique effect on the ion exchange behaviour of metal ions and metallic cationic species. A number of qualitative and quantitative binary, ternary and quaternary separations were achieved in acidic ammonium acetate(22), ammonium format (24), ammonium iodide (23), ammonium sulfosalicilate media which were investigated in laboratories and because of simple relatively weak complexing nature of such media there is a no interference in the estimations of the metal ions. Also, such procedures of separations are not so costly as well as easy to be performed. Therefore in continuation of the interest to investigate and explore another new such medium, i.e., ammonium citrate is selected to study the ion exchange behaviour of a number of metal ions with Amberlite IR120 and Amberlite IRA-400 resins.

In the present study the distribution coefficient for the following cations: Mg(II), Al(III), Mn(II), Fe(II), Fe(III), Ni(II), Co(II), Cu(II), Zn(II), Cd(II) have been determined in aqueous using cation exchanger, Amberlite IR-120 in NH_4^+ - forms and anion exchanger Amberlite IRA-400 in Cl^- form. The results were discussed and the possibilities of the separations were worked out in these media. The compositions of the complex species were also established by the treatment of equilibrium functions, applying the approaches of Schubert and Froneous.

EXPERIMENTAL

Material

- 1. Metal ion Solution:-** Stock solution (0.05-0.1M) of Mg(II), Mn(II), Fe(II), Fe(III), Ni(II), Co(II), Cu(II), Zn(II), Cd(II), Ca(II), were prepared individually from their reagent grade oxide or nitrate (or on some cases sulphates) samples. The compounds used were either of B.D.H. AnalR, E. Merck, S. Merck, G.R. or Harrington Brothers (London) make the prepared solution were then standardized by the method summarized in Table (3.1).
- 2. Disodium salt of ethylenediaminetetraaceticacid (EDTA) :-** As described in chapter 3.
- 3. Ammonium citrate :-** A stock solution 0.1 M was prepared by dissolving 17.29g of citric acid (Qualigens L.R.) in 100cm³ ammonium solution (1N Glaxo Anala R:sp.ge.0.9) in 1:3 ratio to have tri ammonium salt and was standardized by estimating the ammonium amount of the salt (32). The instrument and all other chemicals used were described in chapter-3.
- 4. Resins :-** Amberlite 1R-120 cation exchanger and Amberlite IRA-400 anion exchanger were used as per details, given in chapter-3

CATION AND ANION EXCHANGE DISTRIBUTION STUDIES

The batch equilibration method was employed for determining the distribution coefficients (D). The methodology was followed as described in chapter-3. Aqueous phase mixture solution was having $(\text{NH}_4)_3\text{Cit}(\text{OH})$ concentration range between 1.0×10^{-3} M to 7.0×10^{-3} and constant metal ion concentration to 3.0×10^{-3} M. The air-dried cation exchanger (1.000g) in Cl^- form was added to the mixed aqueous phase.

The flasks were shaken mechanically for 3 hours and it was ascertained that this duration was adequate to attain the equilibrium. Thereafter the resin was filtered off and the metal ion content was determined in an aliquot of the filtrate by titrating against EDTA. Distribution coefficient values were calculated as described in chapter-3. The D-values and percentage loading (%L) for the respective exchanger are given in Table 4.1, 4.3, 4.2, 4.4. and in Fig. 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8.

Table-4.1: Values of Distribution Coefficient (D) of $(\text{NH}_4)_3\text{Cit}(\text{OH})$ media of Amberlite IR - 120 (NH_4^+ - form)

Concentration of [Cit] $\times 10^3$	Distribution Coefficient of Metal Ion [3×10^3]									
	Mg(II)	Mn(II)	Cu(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Co(II)	Ca(II)	Cd(II)
1.00	275.0	400.0	900.0	328.6	400.0	900.0	287.5	500.0	400.0	900.0
1.25	223.9	355.5	733.3	250.6	300.0	700.0	224.2	450.0	326.5	600.0
1.50	172.7	300.0	566.6	172.7	200.0	500.0	160.9	400.0	252.9	300.0
1.75	143.5	244.5	483.3	136.4	157.1	414.3	145.8	364.3	212.8	225.0
2.00	114.3	233.3	400.0	100.0	114.3	328.6	130.8	328.6	172.7	150.0
2.25	107.1	189.5	350.0	93.8	90.5	264.3	112.2	301.8	147.5	121.8
2.50	100.0	172.7	300.0	87.5	66.7	200.0	93.5	275.0	122.2	93.5
2.75	93.8	146.5	268.5	82.0	45.8	165.4	71.8	254.2	104.9	75.7
3.00	87.5	130.8	237.1	76.5	25.0	130.8	50.0	233.3	87.5	57.9
3.25	84.7	114.0	219.3	67.2	21.3	115.4	46.4	203.0	74.8	53.9
3.50	81.8	106.9	201.5	57.9	17.6	100.0	42.9	172.7	62.2	50.0
3.75	79.1	99.8	177.9	50.4	14.4	88.2	39.6	151.7	56.1	46.4
4.00	76.5	87.5	154.2	42.9	11.1	76.5	36.4	130.8	50.0	42.9
4.25	76.5	75.2	135.8	42.9	10.1	67.2	33.4	115.4	50.0	39.6
4.50	76.5	71.4	117.4	42.9	9.1	57.9	30.4	100.0	50.0	36.4
4.75	76.5	67.6	108.4	42.9	7.2	50.4	27.7	88.2	50.0	33.4
5.00	76.5	57.9	99.3	42.9	5.3	42.9	25.0	76.5	50.0	30.4
5.25	76.5	53.5	83.5	42.9	4.4	36.6	22.5	67.2	50.0	27.7
5.50	76.5	50.0	67.6	42.9	3.4	30.4	20.0	57.9	50.0	25.0
5.75	76.5	46.5	55.9	42.9	2.6	25.4	17.7	50.4	50.0	22.5
6.00	76.5	42.9	44.2	42.9	1.7	20.4	15.4	42.9	50.0	20.0
6.25	76.5	39.2	35.3	42.9	1.7	17.9	13.2	38.1	50.0	20.0
6.50	76.5	30.4	26.3	42.9	1.7	15.4	11.1	33.3	50.0	20.0
6.75	76.5	30.4	30.4	42.9	1.7	15.4	9.1	33.3	50.0	20.0
7.00	76.5	30.4	30.4	42.9	1.7	15.4	7.1	33.3	50.0	20.0

Table-4.2 : Values of Percentage Loading (L%) Metal Ion of $(\text{NH}_4)_3\text{Cit}(\text{OH})$ media of Amberlite IR- 120 (NH_4^+ - form)

Concent ration of [Cit] $\times 10^3$	Percentage Loading (L%) Metal Ion									
	Mg(II)	Mn(II)	Cu(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Co(II)	Ca(II)	Cd(II)
1.00	73.3	80.0	80.0	90.0	80.0	90.0	74.2	83.3	80.0	90.0
1.25	69.1	78.0	78.0	88.0	75.0	87.5	69.2	81.8	76.6	85.7
1.50	63.3	75.0	75.0	85.0	66.7	83.3	61.7	80.0	71.7	75.0
1.75	58.9	71.0	71.0	82.9	61.1	80.6	59.3	78.5	68.0	69.2
2.00	53.3	70.0	70.0	80.0	53.3	76.7	56.7	76.7	63.3	60.0
2.25	51.7	65.5	65.5	77.8	47.5	72.5	52.9	75.1	59.6	54.9
2.50	50.0	63.3	63.3	75.0	40.0	66.7	48.3	73.3	55.0	48.3
2.75	48.4	59.4	59.4	72.9	31.4	62.3	41.8	71.8	51.2	43.1
3.00	46.7	56.7	56.7	70.3	20.0	56.7	33.3	70.0	46.7	36.7
3.25	45.8	53.3	53.3	68.7	17.6	53.6	31.7	67.0	42.8	35.0
3.50	45.0	51.7	51.7	66.8	15.0	50.0	30.0	63.3	38.3	33.3
3.75	44.2	49.9	49.9	64.0	12.6	46.9	28.4	60.3	35.9	31.7
4.00	43.3	46.7	46.7	60.7	10.0	43.3	26.7	56.7	33.3	30.0
4.25	43.3	42.9	42.9	57.6	9.2	40.2	25.0	53.6	33.3	28.4
4.50	43.3	41.7	41.7	54.0	8.3	36.7	23.3	50.0	33.3	26.7
4.75	43.3	40.3	40.3	52.0	6.7	33.5	21.7	46.9	33.3	25.0
5.00	43.3	36.7	36.7	49.8	5.0	30.0	20.0	43.3	33.3	23.3
5.25	43.3	34.9	34.9	45.5	4.2	26.8	18.4	40.2	33.3	21.7
5.50	43.3	33.3	33.3	40.3	3.3	23.3	16.7	36.7	33.3	20.0
5.75	43.3	31.7	31.7	35.9	2.5	20.3	15.0	33.5	33.3	18.4
6.00	43.3	30.0	30.0	30.7	1.7	17.0	13.3	30.0	33.3	16.7
6.25	43.3	28.2	28.2	26.1	1.7	15.2	11.7	27.6	33.3	16.7
6.50	43.3	23.3	23.3	20.8	1.7	13.3	10.0	25.0	33.3	16.7
6.75	43.3	23.3	23.3	23.3	1.7	13.3	8.4	25.0	33.3	16.7
7.00	43.3	23.3	23.3	23.3	1.7	13.3	6.7	25.0	33.3	16.7

Table-4.3: Values of Distribution Coefficient (D) of $(\text{NH}_4)_3\text{Cit}(\text{OH})$ media of Amberlite IRA - 400 (Cl^- - form)

Concent ration of [Cit] $\times 10^3$	Distribution Coefficient of Metal Ion $[3 \times 10^3]$									
	Mg(II)	Mn(II)	Cu(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Co(II)	Ca(II)	Cd(II)
1.00	36.4	25.0	11.1	30.4	25.0	11.1	36.4	20.0	25.0	11.1
1.25	47.1	29.2	14.4	44.2	37.5	15.6	49.3	22.5	32.3	22.2
1.50	57.9	33.3	17.6	57.9	50.0	20.0	62.2	25.0	39.5	33.3
1.75	72.7	38.1	21.3	71.4	85.0	25.0	69.3	27.7	48.7	50.0

2.00	87.5	42.9	25.0	85.0	120.0	30.0	76.5	30.4	57.9	66.7
2.25	93.8	50.4	29.2	99.6	166.0	40.0	91.7	33.4	69.9	86.8
2.50	100.0	57.9	33.3	114.3	212.0	50.0	106.9	36.4	81.8	106.9
2.75	107.1	67.2	37.8	132.1	306.0	63.2	133.9	39.6	98.0	139.8
3.00	114.3	76.5	42.2	150.0	400.0	76.5	161.0	42.9	114.3	172.7
3.25	118.3	85.0	45.9	161.4	483.3	88.2	197.2	50.4	137.6	186.4
3.50	122.2	93.5	49.6	172.7	566.7	100.0	233.3	57.9	160.9	200.0
3.75	126.5	103.9	57.2	191.4	712.3	115.4	254.2	67.1	180.4	237.5
4.00	130.8	114.3	64.8	210.0	858.0	130.8	275.0	76.4	200.0	275.0
4.25	130.8	127.1	75.0	221.7	1074.5	151.7	301.8	88.2	200.0	301.8
4.50	130.8	140.0	85.2	233.3	1291.0	172.7	328.6	100.0	200.0	328.6
4.75	130.8	156.4	92.9	233.3	1595.5	203.0	364.3	115.4	200.0	364.3
5.00	130.8	172.7	100.6	233.3	1900.0	233.3	400.0	130.8	200.0	400.0
5.25	130.8	186.4	124.3	233.3	2400.0	281.0	450.0	151.7	200.0	450.0
5.50	130.8	200.0	147.9	233.3	2900.0	328.6	500.0	172.7	200.0	500.0
5.75	130.8	216.7	187.0	233.3	4400.0	414.3	575.0	203.0	200.0	500.0
6.00	130.8	233.3	226.1	233.3	5900.0	500.0	650.0	233.3	200.0	500.0
6.25	130.8	280.9	303.0	233.3	5900.0	575.0	775.0	266.7	200.0	500.0
6.50	130.8	328.6	380.0	233.3	5900.0	650.0	900.0	300.0	200.0	500.0
6.75	130.8	328.6	380.0	233.3	5900.0	650.0	1150.0	300.0	200.0	500.0
7.00	130.8	328.6	380.0	233.3	5900.0	650.0	1400.0	300.0	200.0	500.0

Table-4.4 : Values of Percentage Loading (L%) Metal Ion of (NH₄)₃Cit(OH)media of Amberlite IRA- 400 (Cl⁻ form)

Concentration of [Cit] x 10 ³	Percentage Loading (L%) Metal Ion [3x10 ³]									
	Mg(II)	Mn(II)	Cu(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Co(II)	Ca(II)	Cd(II)
1.00	26.7	20.0	10.0	23.3	20.0	10.0	26.7	16.7	20.0	10.0
1.25	32.0	22.6	12.6	30.6	27.3	13.5	33.0	18.4	24.4	18.2
1.50	36.7	25.0	15.0	36.7	33.3	16.7	38.3	20.0	28.3	25.0
1.75	42.1	27.6	17.6	41.7	45.9	20.0	40.9	21.7	32.8	33.3
2.00	46.7	30.0	20.0	45.9	54.5	23.1	43.3	23.3	36.7	40.0
2.25	48.4	33.5	22.6	49.9	62.4	28.6	47.8	25.0	41.1	46.5
2.50	50.0	36.7	25.0	53.3	67.9	33.3	51.7	26.7	45.0	51.7
2.75	51.7	40.2	27.4	56.9	75.4	38.7	57.3	28.4	49.5	58.3
3.00	53.3	43.3	29.7	60.0	80.0	43.3	61.7	30.0	53.3	63.3
3.25	54.2	45.9	31.5	61.7	82.9	46.9	66.3	33.5	57.9	65.1
3.50	55.0	48.3	33.2	63.3	85.0	50.0	70.0	36.7	61.7	66.7
3.75	55.8	51.0	36.4	65.7	87.7	53.6	71.8	40.2	64.3	70.4
4.00	56.7	53.3	39.3	67.7	89.6	56.7	73.3	43.3	66.7	73.3
4.25	56.7	56.0	42.9	68.9	91.5	60.3	75.1	46.9	66.7	75.1

Fig. 4.1 Plot of Distribution Coefficient (D) vs [Cit] for Amberlite IR-120

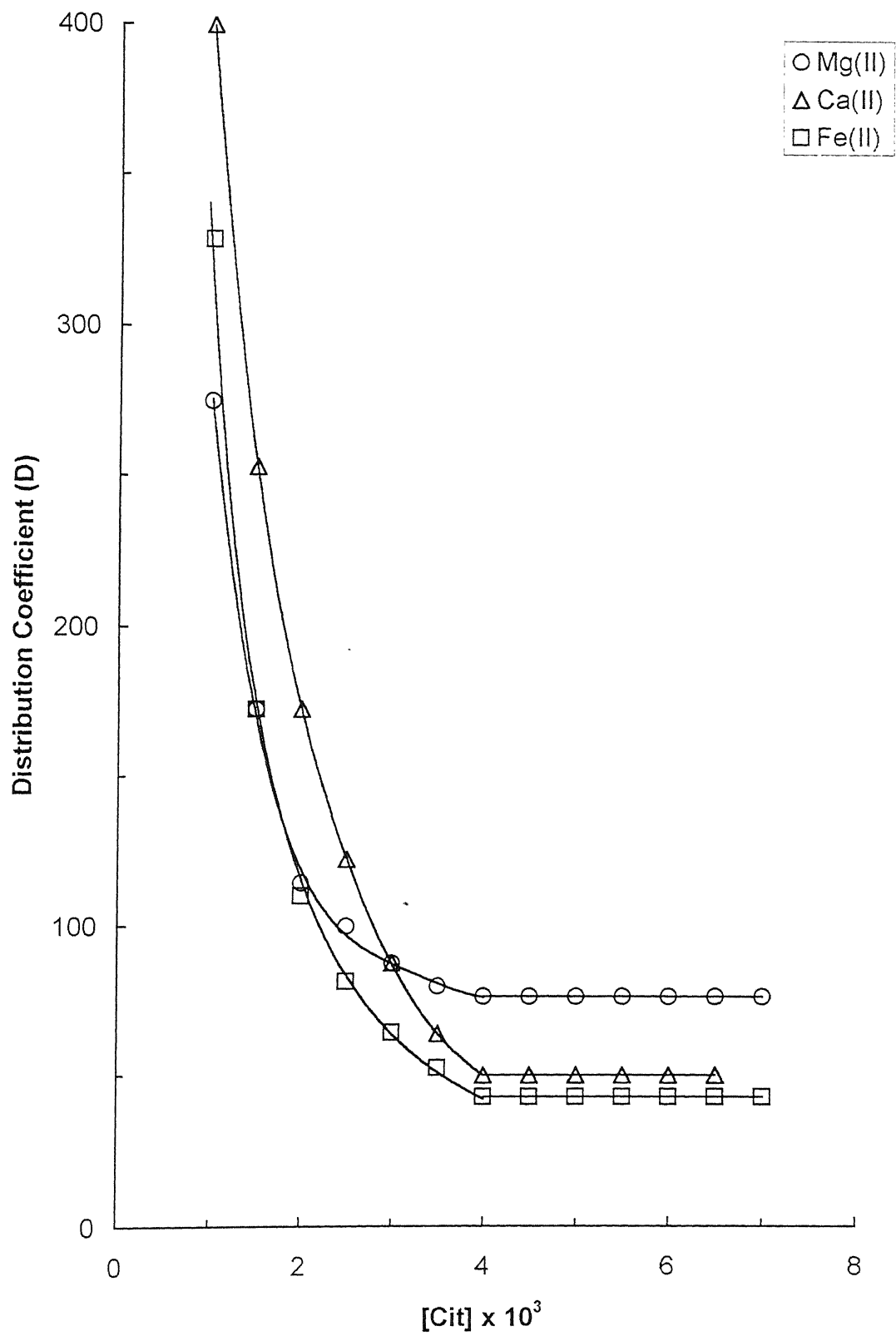


Fig. 4.2 Plot of Distribution Coefficient (D) vs [Cit] for Amberlite IR-120

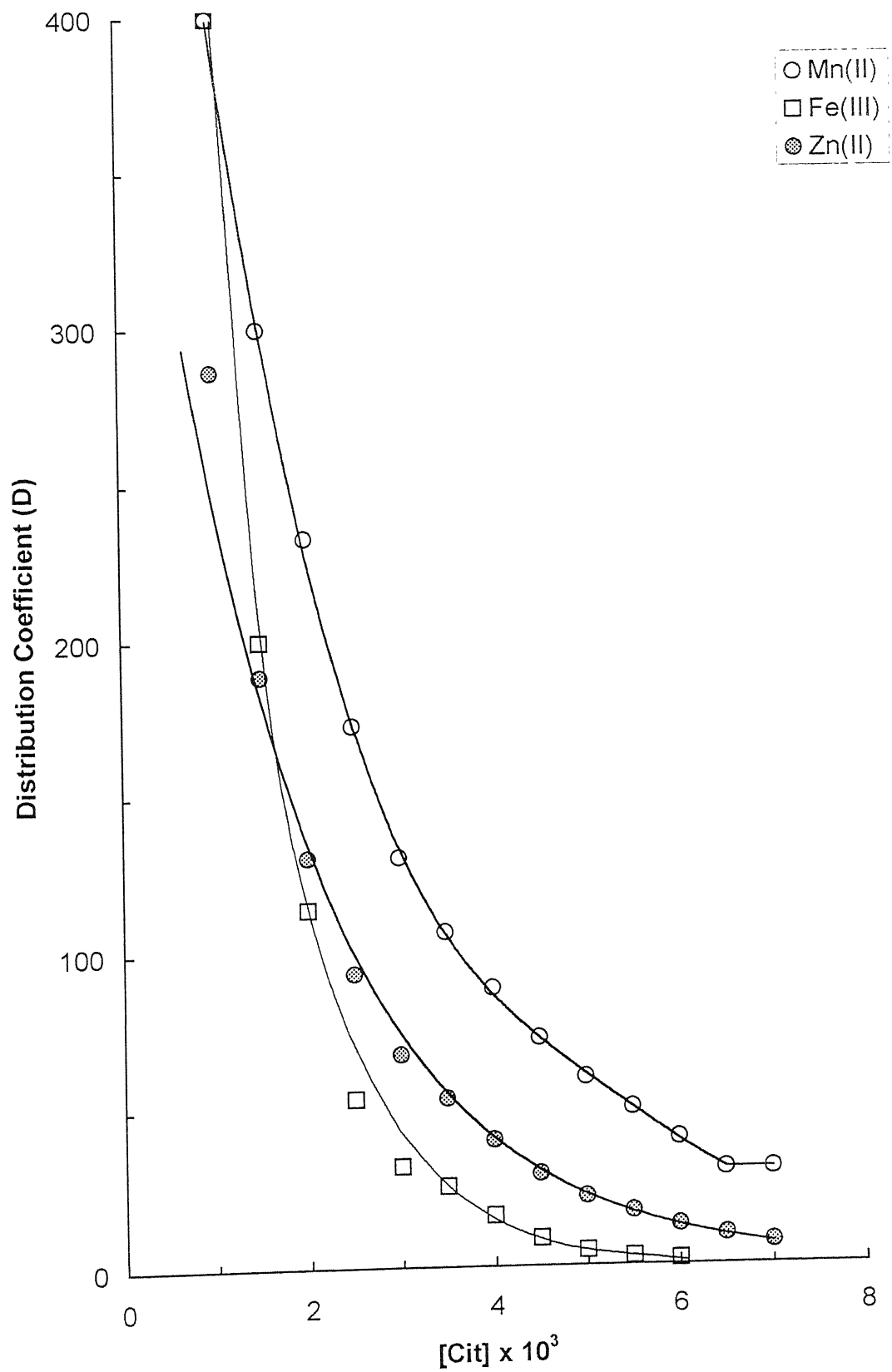


Fig. 4.3 Plot of Distribution Coefficient (D) vs [Cit] for Amberlite IR-120

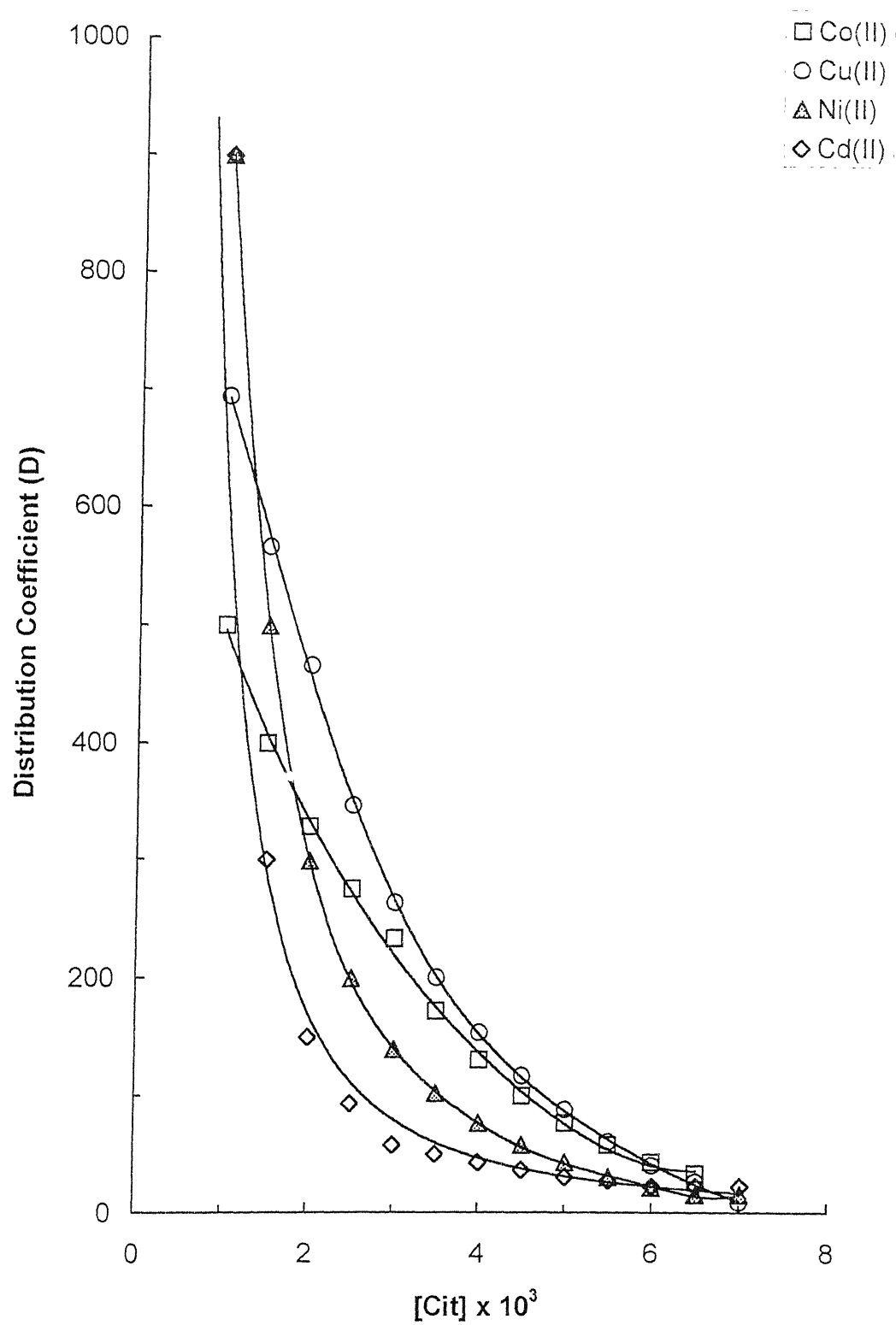


Fig. 4.4 Percentage Loading(%L) vs [Cit]
for Amberlite IR-120

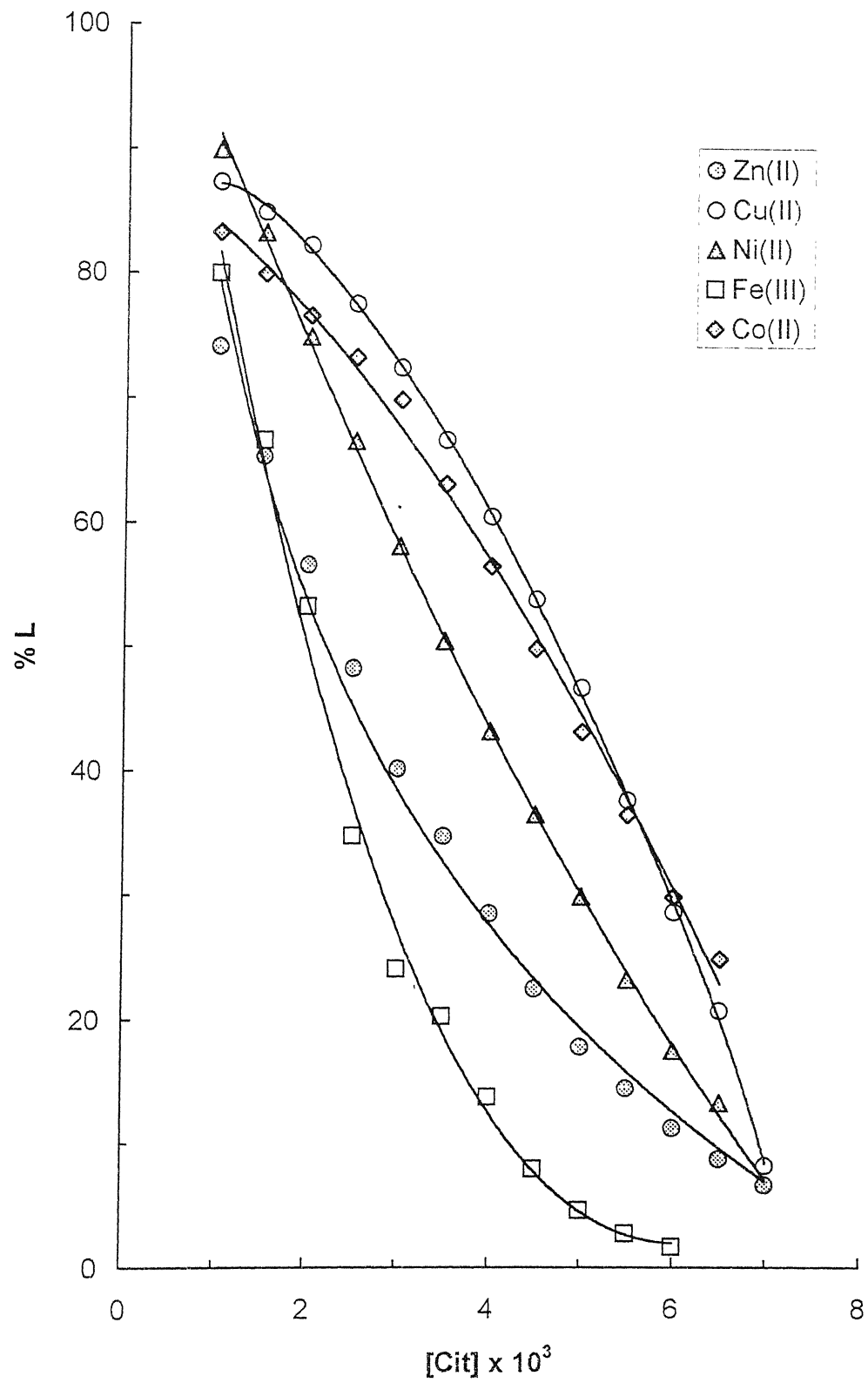


Fig.4.5 Percentage Loading(%L) vs [Cit] for
Amberlite IR-120

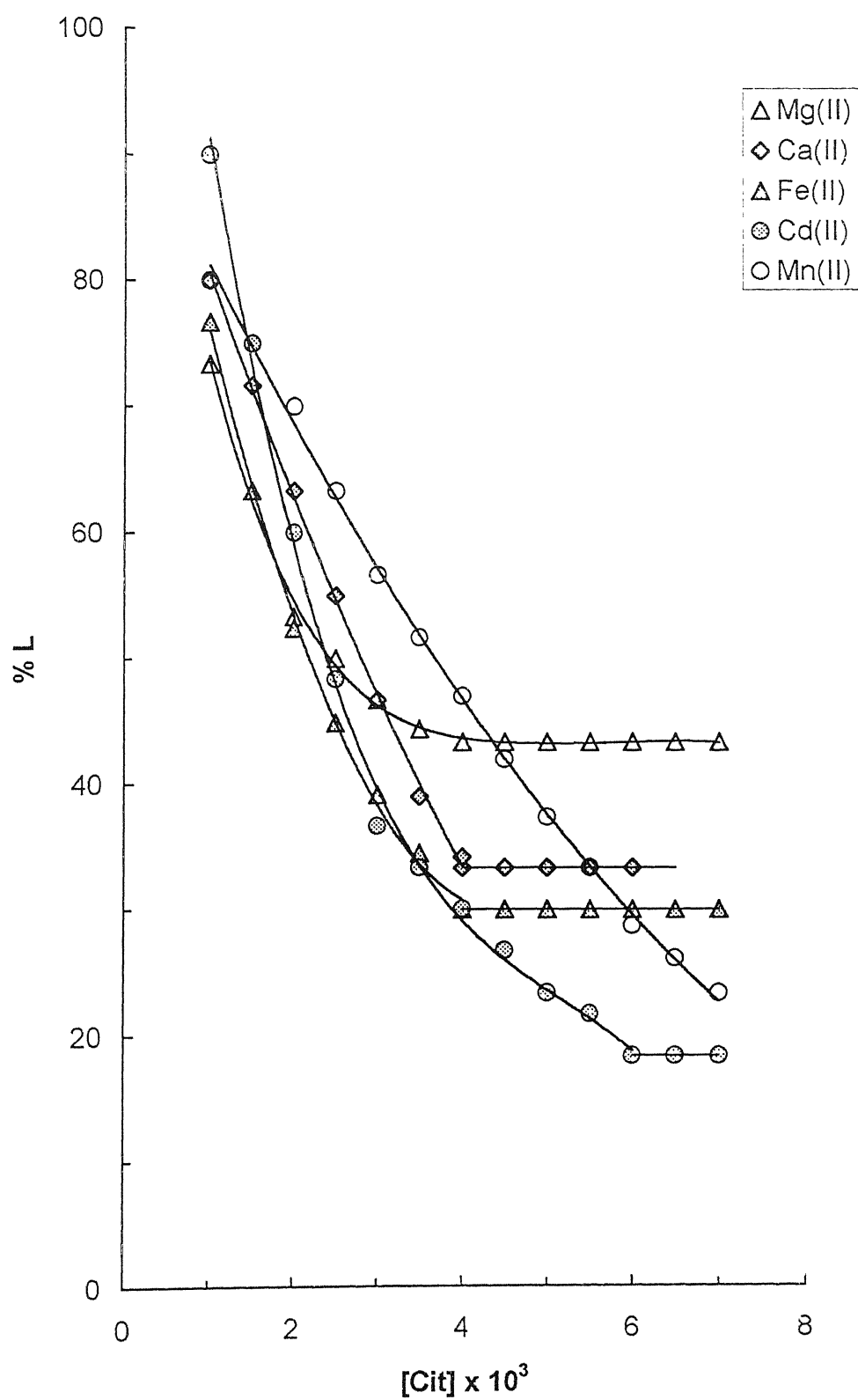


Fig. 4.6 Plot of Distribution Coefficient (D) vs [Cit]
for Amberlite IRA-400

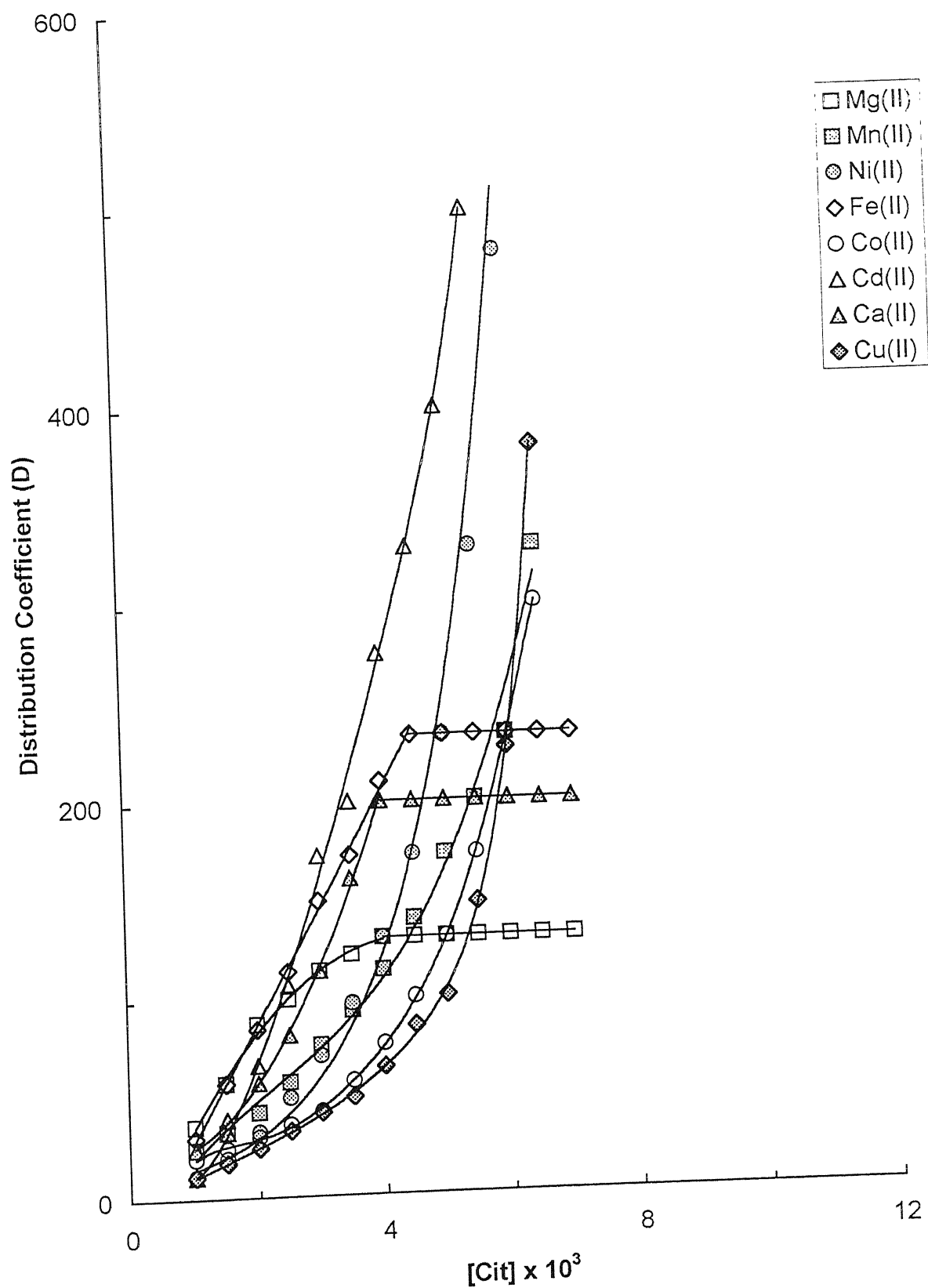


Fig.4.7 Plot of Distribution Coefficient (D) vs [Cit] for Amberlite IRA-400

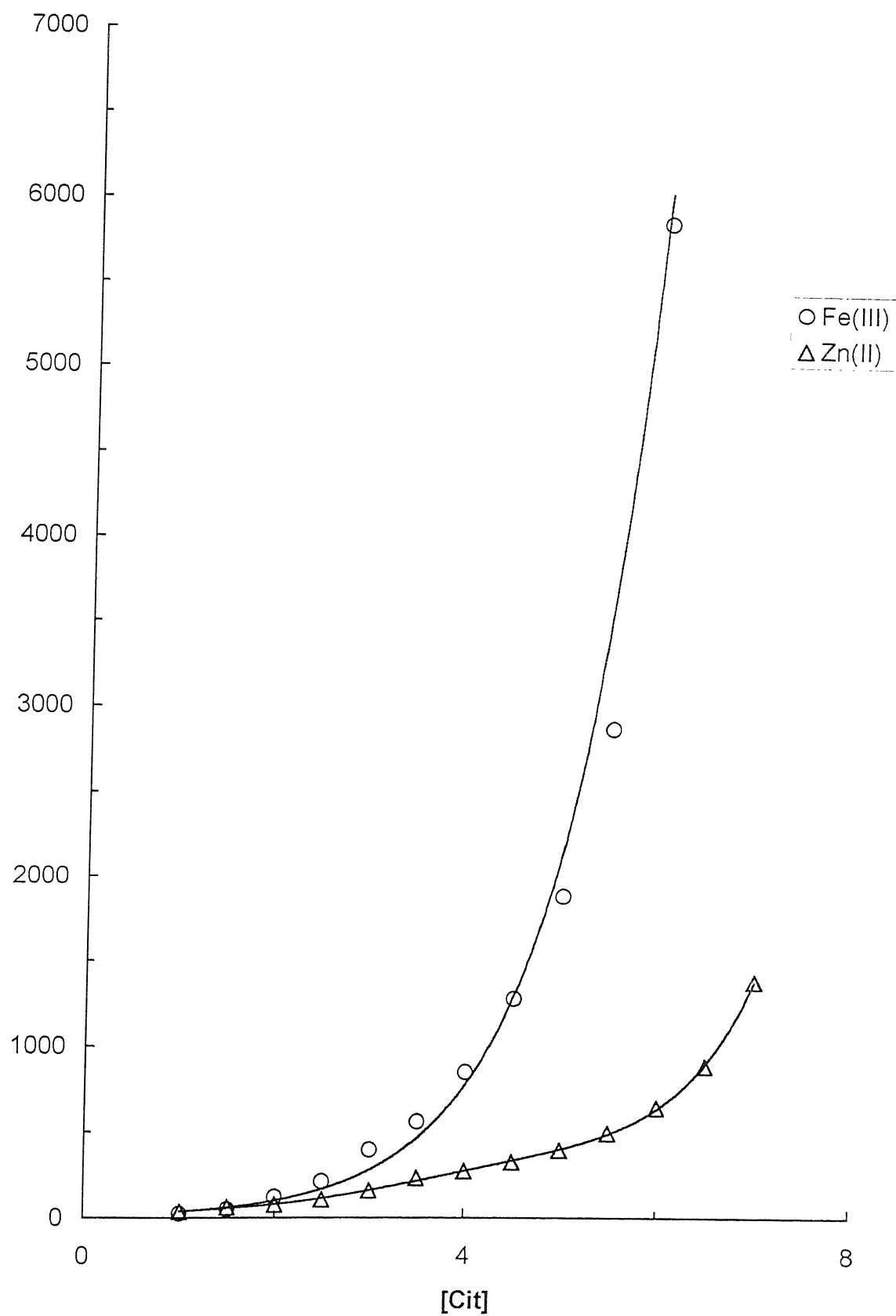
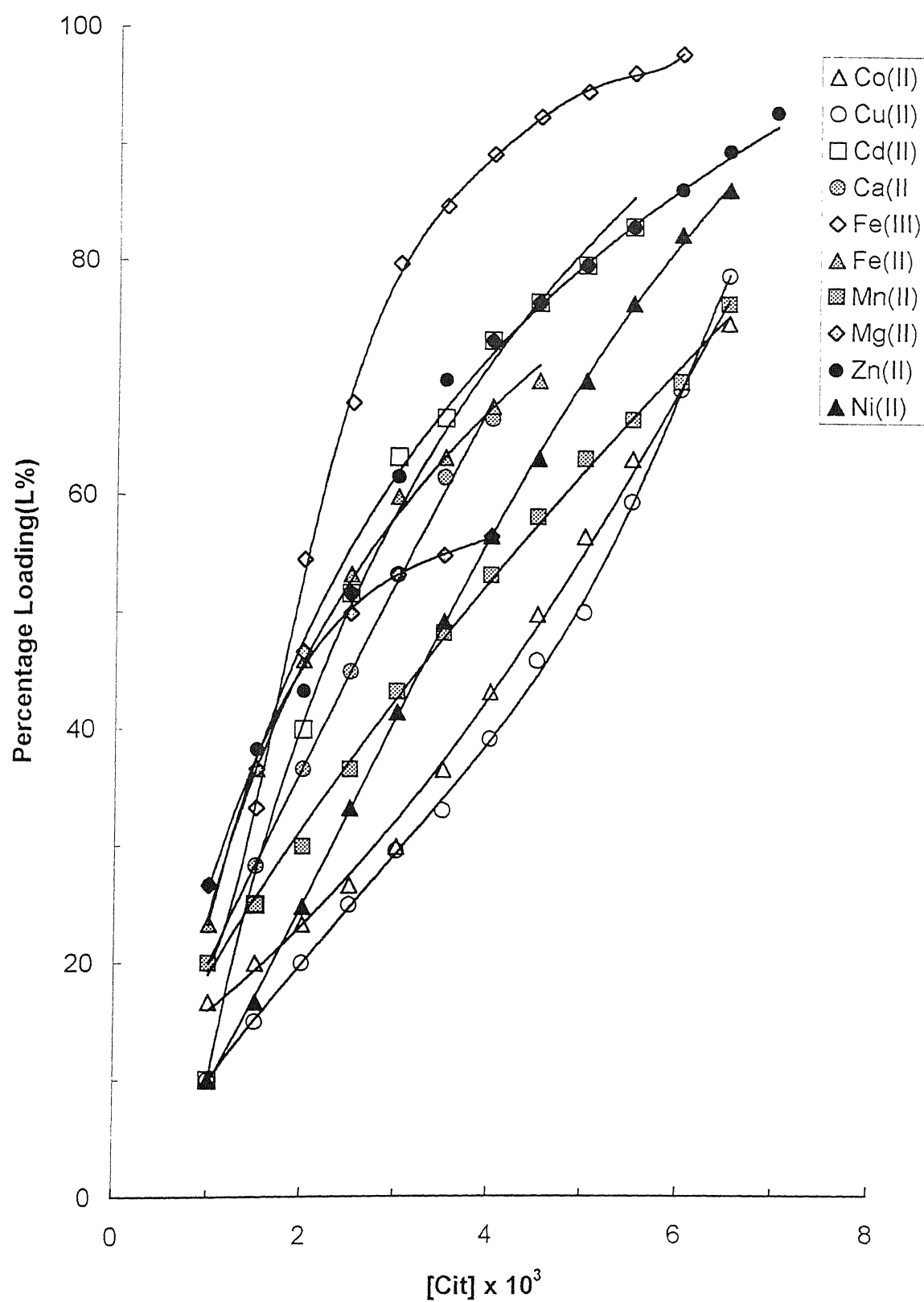


Fig. 4.8 Percentage Loading(L%) vs [Cit]



4.50	56.7	58.3	46.0	70.0	92.8	63.3	76.7	50.0	66.7	76.7
4.75	56.7	61.0	48.2	70.0	94.1	67.0	78.5	53.6	66.7	78.5
5.00	56.7	63.3	50.1	70.0	95.0	70.0	80.0	56.7	66.7	80.0
5.25	56.7	65.1	55.4	70.0	96.0	73.7	81.8	60.3	66.7	81.8
5.50	56.7	66.7	59.7	70.0	96.7	76.7	83.3	63.3	66.7	83.3
5.75	56.7	68.4	65.2	70.0	97.8	80.6	85.2	67.0	66.7	83.3
6.00	56.7	70.0	69.3	70.0	98.3	83.3	86.7	70.0	66.7	83.3
6.25	56.7	73.7	75.2	70.0	98.3	85.2	88.6	72.7	66.7	83.3
6.50	56.7	76.7	79.2	70.0	98.3	86.7	90.0	75.0	66.7	83.3
6.75	56.7	76.7	79.2	70.0	98.3	86.7	92.0	75.0	66.7	83.3
7.00	56.7	76.7	79.2	70.0	98.3	86.7	93.3	75.0	66.7	83.3

RESULT AND DISCUSSION

The observation of the experiments perform for the cation exchange distribution study indicate for each individual metal that its sorption gradually decreases with the increase in the concentration of $(\text{NH}_4)_3\text{Cit}(\text{OH})$. But the nature of decreasing pattern of each curve varies metal to metal. It is the complexation by the citrate with the metal ion is responsible for the decrease in the sorption of the individual metal, because the cation exchanger was taken in the NH_4^+ - form which rules out the possibility of any competitive sorption by it (NH_4^+ cation). This medium $(\text{NH}_4)_3\text{Cit}(\text{OH})$ may also be considered as having a strong buffering activity due to its formation by the interaction on a weak acid and a weak base . Citric acid is having three dissociable carboxylic acid group and therefore the salt $(\text{NH}_4)_3\text{Cit}(\text{OH})$ possess three NH_4^+ ions and the activity contributed by ammonium radical thus enhanced incomparison to the salt having single ammonium ion. It has also been observed that the aqueous phase mixture solution has the pH 7.6 before equilibration and 8.02 after the equilibration. But even the metal ion iron(III) had not shown any indication of the hydrolysis, confirming the dominance of complexation by the citrate. A little enhancement of pH from the initial non equilibration aqueous phase solution to equilibrated solution may be considered due to change in ionic association processes simultaneously going on in the aqueous solution phase, sorbed solution presented in the resin, and the solid exchanger phase. This little pH change may not contributing effectively to the exchange equilibrium or the sorptions of the exchanging metal ion species.

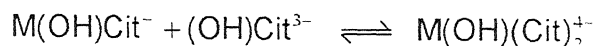
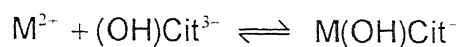
Prior to investigation of above described systems, the studies were carried out with Zn^{2+} using a medium of constant NH_4OAc and varying the citric acid as in case of system worked out and presented in chapter-3, but these could not be investigated further due to observed constant sorption of the metal ion species in the resin phase, i.e., showing no gradual decrease or increase in the distribution coefficient values or because of the no appreciable change in the complexation tendencies by the citrate given table .

Table-4.5

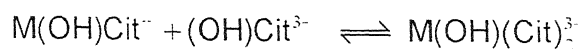
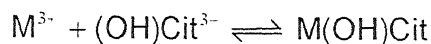
Zn(II) x 10³M	NH₄OAc x10³M	Citric Acid x10³	D
3.0	3.0	1.0	1400.0
3.0	3.0	2.0	650.0
3.0	3.0	3.0	328.5
3.0	3.0	4.0	328.5
3.0	3.0	5.0	328.5
3.0	3.0	6.0	328.5
3.0	3.0	7.0	328.5
3.0	3.0	8.0	328.5
3.0	3.0	9.0	328.5
3.0	3.0	10.0	328.5

Apart other metal ions Zn (II) has shown continuously decrease in the D-value throughout the investigated range of $(\text{NH}_4)_3\text{Cit}(\text{OH})$ concentration range. All other metal ions have also shown a decrease in the D-values but at a certain $(\text{NH}_4)_3\text{Cit}(\text{OH})$ concentration D-values become constant, that means from that particular $(\text{NH}_4)_3\text{Cit}(\text{OH})$ concentration onward the complexation of the metal with the citrate becomes almost constant resulting to same sorption or D-value or it may be considered as that the complexation equilibrium of all the metal ions except Zn(II) has reached at a particular $(\text{NH}_4)_3\text{Cit}(\text{OH})$ concentration. The metal ions, Pb(II), Th(II) and La(II) could not be investigated due the precipitation in the studied ammonium citrate media.

The studies were also made from these distribution coefficient data for evaluating the ion exchange equilibrium constant for the metal citrate complexation systems. The probable metal ion citrate equilibrium reactions for the bivalent and trivalent metal ion may be represented as-



And,



The interaction of the anionic metal-citrate species with the NH_4^+ ion may exist due to ion association but for evaluation of formation constant such considerations are ignored. The equilibrium formation constant are given as,

$$K_1 = [M(Cit)(OH)] / [M][(OH)Cit]$$

$$K_2 = [M\{Cit(OH)\}_2] / [M(OH)Cit][(OH)Cit]$$

$$\beta_2 = [M\{Cit(OH)\}_2] / [M][(OH)Cit]^2$$

$$\beta_n = [M\{Cit(OH)\}_{n-1}] / [M][(OH)Cit]^n$$

The overall or gross metal ion exchange distribution is represented as (considering the maximum association of the citrate ligand (L), i.e. n=2),

$$D = \frac{[M]_r}{([M] + \beta_1[M][L] + \beta_2[M][L]^2)} \quad \text{————— (1)}$$

$$D = \frac{[M]_r}{[M]} \left(\frac{1}{1 + \beta_1[L] + \beta_2[L]^2} \right) \quad \text{————— (2)}$$

The factor, $([M]_r / [M])$, is the distribution of metal species in absence of the ligand, and is usually designated as D_o (i.e., distribution coefficient of free metal ion species), then

$$\frac{D_o}{D} = 1 + \sum_{n=1}^{N=n+2} \beta_n [L]^n \quad \text{————— (3)}$$

Or
$$\left\{ \frac{(D_o / D - 1)}{[L]} \right\} = \beta_1 + \beta_2 [L] \quad \text{————— (4)}$$

Or
$$\left\{ \frac{(D_o / D - 1)}{[L]^2} \right\} = \beta_1 \frac{1}{[L]} + \beta_2 \quad \text{————— (5)}$$

The values of β_1 is obtain as the intercept plot, of $\left\{ \frac{(D_o/D-1)}{[L]} \right\}$ Vs $[L]$ as a limiting value, and the value of β_2 is obtained as the intercept plot of $\left\{ \frac{(D_o/D-1)}{[L]^2} \right\}$ Vs $1/[L]$ as a limiting value. The various calculated data are given in Tables 4.5, 4.6.

The complexation tendencies of the citrate differ with respect to concentration of the citrate, the nature of the involve metal ion, and the charge present on the metal ion species. Mg(II), Zn(II) have shown relatively lowest sorption on to the cation exchanger at 1.00×10^{-3} M citrate concentrations clearly showing the strong complexation highest sorptions, while highest sorption have been observed for Cu(II), Ni(II), and Cd(II) at the same citrate concentration. On the contrary increasing the citrate amounts the transition metal ion species have shown more and more stronger complexation by the citrate related to magnesium or calcium. This behaviours not abnormal and is with the agreement of the characteristics of p and d- block element. Also, except in case of Zn(II) all other metal ion studied have shown the constancy after a particular citrate concentration from there the D- values become constant.

Table 4.5:- Shubert's Function and Other Calculated Variables of metal ions in $(\text{NH}_4)_3\text{Cit}(\text{OH})$ media on Amberlite IR -120(NH_4^+ -form)

[Zn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$] System				
[Cit] X 10^3M	($D_o/D-1$)	($D_o/D-1$)/ [Cit] x 10^{-4}	1/[Cit] X 10^{-3}M	($D_o/D-1$)/ [Cit]² x 10^{-6}
1.0	6.0	0.60	1.00	1.43
1.5	9.6	0.64	0.67	1.19
2.0	14.3	0.71	0.50	1.08
2.5	20.4	0.82	0.40	1.03
3.0	28.6	0.95	0.33	1.03
3.5	36.4	1.04	0.29	0.98
4.0	48.8	1.22	0.25	1.02
4.5	67.5	1.50	0.22	1.13
5.0	90.7	1.81	0.20	1.23
5.5	116.6	2.12	0.18	1.32
6.0	156.5	2.61	0.17	1.49

6.5	207.3	3.19	0.15	1.69
7.0	279.1	3.99	0.14	1.96
[Ni(II)- (NH₄)₃Cit(OH)] System				
[Cit] X 10³M	(D_o/ D-1)	(D_o/D-1)/ [Cit] x10⁻⁴	1/[Cit] X 10⁻³M	(D_o/D-1)/ [Cit]² x10⁻⁶
1.0	1.78	0.18	1.00	1.78
1.5	4.00	0.27	0.67	1.78
2.0	6.61	0.33	0.50	1.84
2.5	11.50	0.46	0.40	1.84
3.0	18.12	0.69	0.33	1.88
3.5	24.00	0.69	0.29	1.96
4.0	31.69	0.79	0.25	1.98
4.5	42.21	0.94	0.22	2.08
5.0	57.34	1.15	0.20	2.29
5.5	81.16	1.48	0.18	2.68
6.0	121.55	1.93	0.17	3.22
6.5	161.55	2.49	0.15	3.82
7.0	161.55	2.31	0.14	3.30
[Mn(II)- (NH₄)₃Cit(OH)] System				
[Cit] X 10³M	(D_o/ D-1)	(D_o/D-1)/ [Cit] x10⁻³	1/[Cit] X 10⁻³M	(D_o/D-1)/ [Cit]² x10⁻⁵
1.0	0.92	0.92	1.00	9.23
1.5	1.56	1.04	0.67	6.95
2.0	2.30	1.15	0.50	5.74
2.5	3.45	1.38	0.40	5.53
3.0	4.88	1.63	0.33	5.43
3.5	6.20	1.77	0.29	5.06
4.0	7.68	1.92	0.25	4.80
4.5	9.64	2.14	0.22	4.76
5.0	11.88	2.38	0.20	4.75
5.5	14.38	2.62	0.18	4.76
6.0	18.12	3.02	0.17	5.03
6.5	24.28	3.74	0.15	5.75
7.0	24.28	3.47	0.14	4.95
[Co(II)- (NH₄)₃Cit(OH)] System				
[Cit] X 10³M	(D_o/ D-1)	(D_o/D-1)/ [Cit] x10⁻³	1/[Cit] X 10⁻³M	(D_o/D-1)/ [Cit]² x10⁻⁵
1.0	1.86	1.86	1.00	1.8.6
1.5	2.57	1.71	0.67	1.14
2.0	3.35	1.67	0.50	8.37
2.5	4.19	1.68	0.40	6.71

3.0	5.12	1.71	0.33	5.69
3.5	7.30	2.08	0.29	5.96
4.0	9.93	2.48	0.25	6.20
4.5	13.29	2.95	0.22	6.56
5.0	17.68	3.54	0.20	7.07
5.5	23.68	4.30	0.18	7.83
6.0	32.34	5.39	0.17	8.98
6.5	41.86	6.44	0.15	9.91
[Cu(II)- (NH₄)₃Cit(OH)] System				
[Cit] X 10³M	(D_o/ D-1)	(D_o/D-1)/ [Cit] x10⁻³	1/[Cit] X 10⁻³M	(D_o/D-1)/ [Cit]² x10⁻⁵
1.0	0.51	0.51	1.00	5.06
1.5	0.85	0.56	0.67	3.76
2.0	1.24	0.62	0.50	3.10
2.5	2.01	0.81	0.40	3.22
3.0	2.96	0.99	0.33	3.29
3.5	4.20	1.20	0.29	3.43
4.0	5.78	1.45	0.25	3.61
4.5	7.91	1.76	0.22	3.91
5.0	10.87	2.17	0.20	4.35
5.5	16.20	2.95	0.18	5.36
6.0	24.91	4.15	0.17	6.92
6.5	38.76	5.96	0.15	9.17
7.0	115.24	16.46	0.14	2.35
[Cd(II)- (NH₄)₃Cit(OH)] System				
[Cit] X 10³M	(D_o/ D-1)	(D_o/D-1)/ [Cit] x10⁻³	1/[Cit] X 10⁻³M	(D_o/D-1)/ [Cit]² x10⁻⁶
1.0	0.51	5.88	1.00	5.88
1.5	0.85	13.10	0.67	8.74
2.0	1.24	20.15	0.50	10.08
2.5	2.01	26.11	0.40	10.44
3.0	2.96	35.34	0.33	11.78
3.5	4.20	35.12	0.29	10.03
4.0	5.78	35.86	0.25	8.96
4.5	7.91	37.61	0.22	8.36
5.0	10.87	40.52	0.20	8.10
5.5	16.20	9.67	0.18	7.36
6.0	24.91	45.73	0.17	7.62
6.5	38.76	42.21	0.15	6.49
7.0	115.24	39.20	0.14	5.60

Table 4.6:- Shubert's Function and Other Calculated Variables of metal ions in $(\text{NH}_4)_3\text{Cit}(\text{OH})$ media on Amberlite IR-120(NH_4^+ -form)

[Ca(II) - $(\text{NH}_4)_3\text{Cit}(\text{OH})$] System			[Mg(II) - $(\text{NH}_4)_3\text{Cit}(\text{OH})$] System		
[Cit] X 10^3M	$(D_o/D-1)$	$(D_o/D-1) / [\text{Cit}] \times 10^{-3}$	[Cit] X 10^3M	$(D_o/D-1)$	$(D_o/D-1) / [\text{Cit}] \times 10^{-4}$
1.0	1.27	1.27	1.0	17.2	1.72
1.5	2.59	1.73	1.5	27.9	1.86
2.0	4.26	2.13	2.0	42.8	2.14
2.5	6.44	2.58	2.5	49.0	1.96
3.0	9.39	3.13	3.0	56.1	1.87
3.5	13.20	3.77	3.5	61.7	1.76
4.0	17.18	4.30	4.0	64.4	1.61
4.5	17.18	3.82	4.5	64.4	1.43
5.0	17.18	3.44	5.0	64.4	1.29
5.5	17.18	3.12	5.5	64.4	1.17
6.0	17.18	2.86	6.0	64.4	1.07
6.5	17.18	2.64	6.5	64.4	0.99
7.0	17.18	2.64	7.0	64.4	0.92

[Fe(II) - $(\text{NH}_4)_3\text{Cit}(\text{OH})$] System		
[Cit] X 10^3M	$(D_o/D-1)$	$(D_o/D-1) / [\text{Cit}] \times 10^{-3}$
1.0	2.58	2.6
1.5	5.81	3.9
2.0	10.76	4.7
2.5	13.47	5.4
3.0	17.27	5.8
3.5	21.37	6.1
4.0	26.46	6.6
4.5	26.46	5.9
5.0	26.46	5.3
5.5	26.46	4.8
6.0	26.46	4.4
6.5	26.46	4.1

Fig. 4.9 Plot of Mn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system
 $(D_o/D-1)/[\text{Cit}]$ vs $[\text{Cit}]$

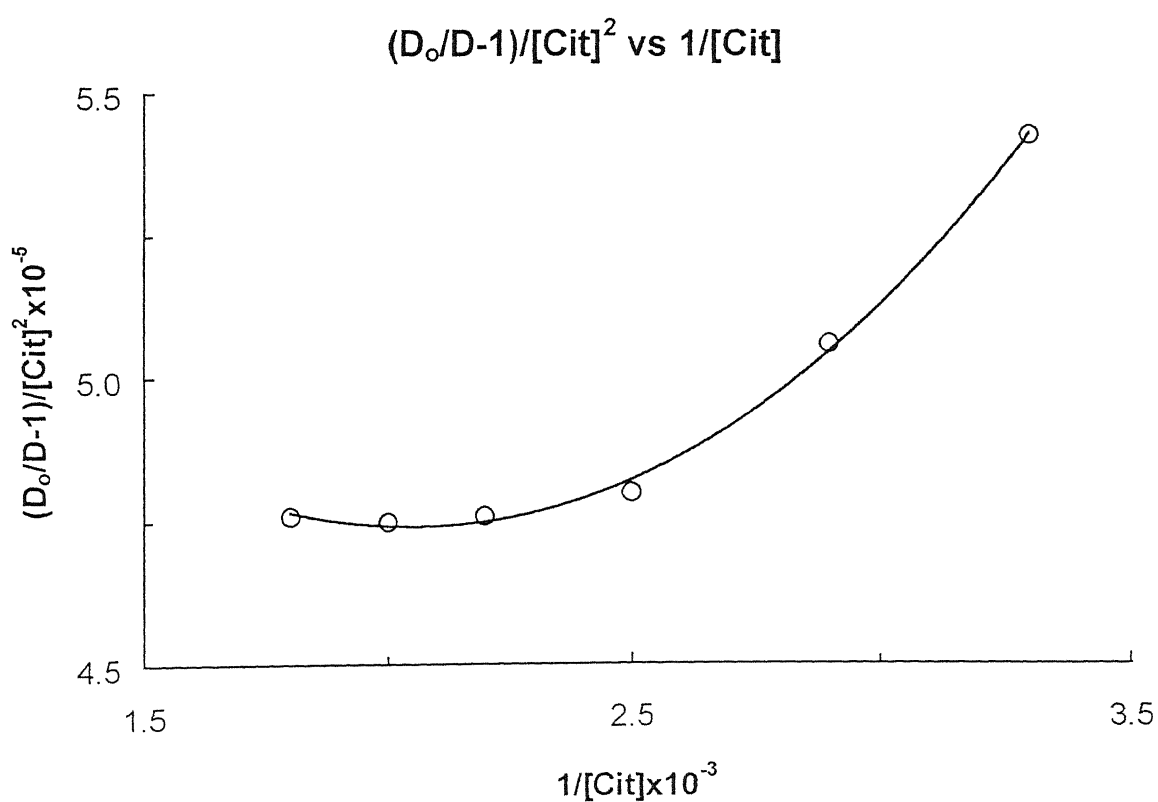
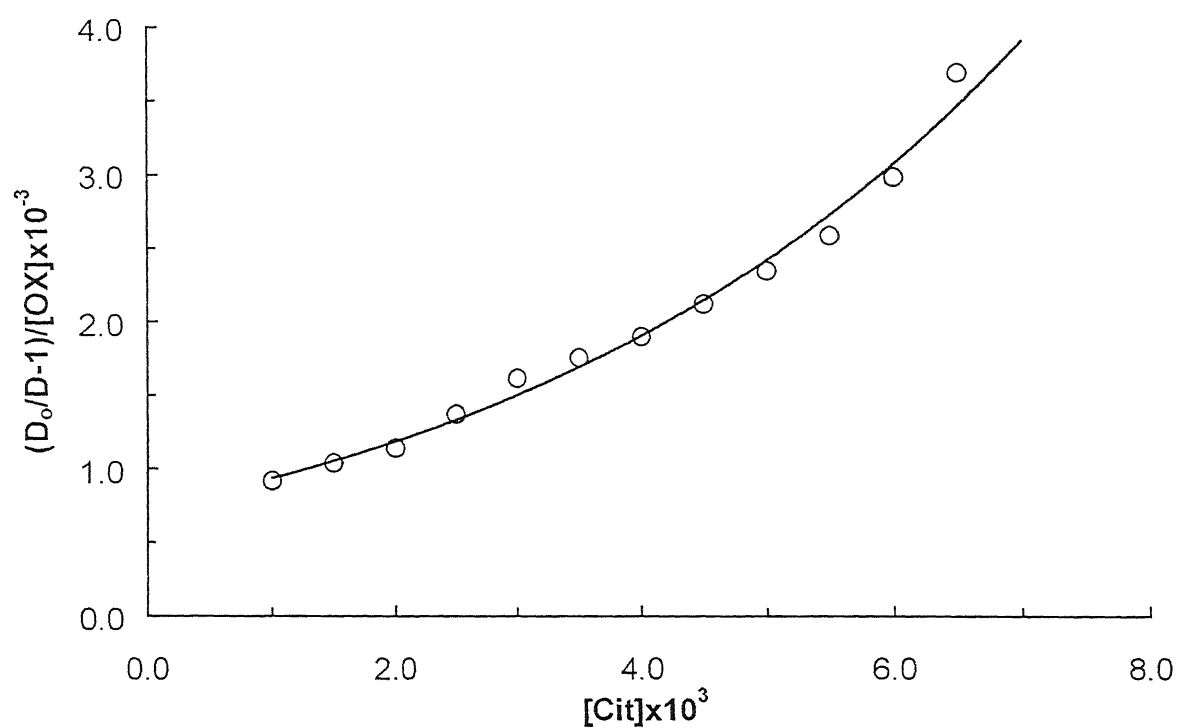


Fig. 4.10 Plot of Fe(III)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

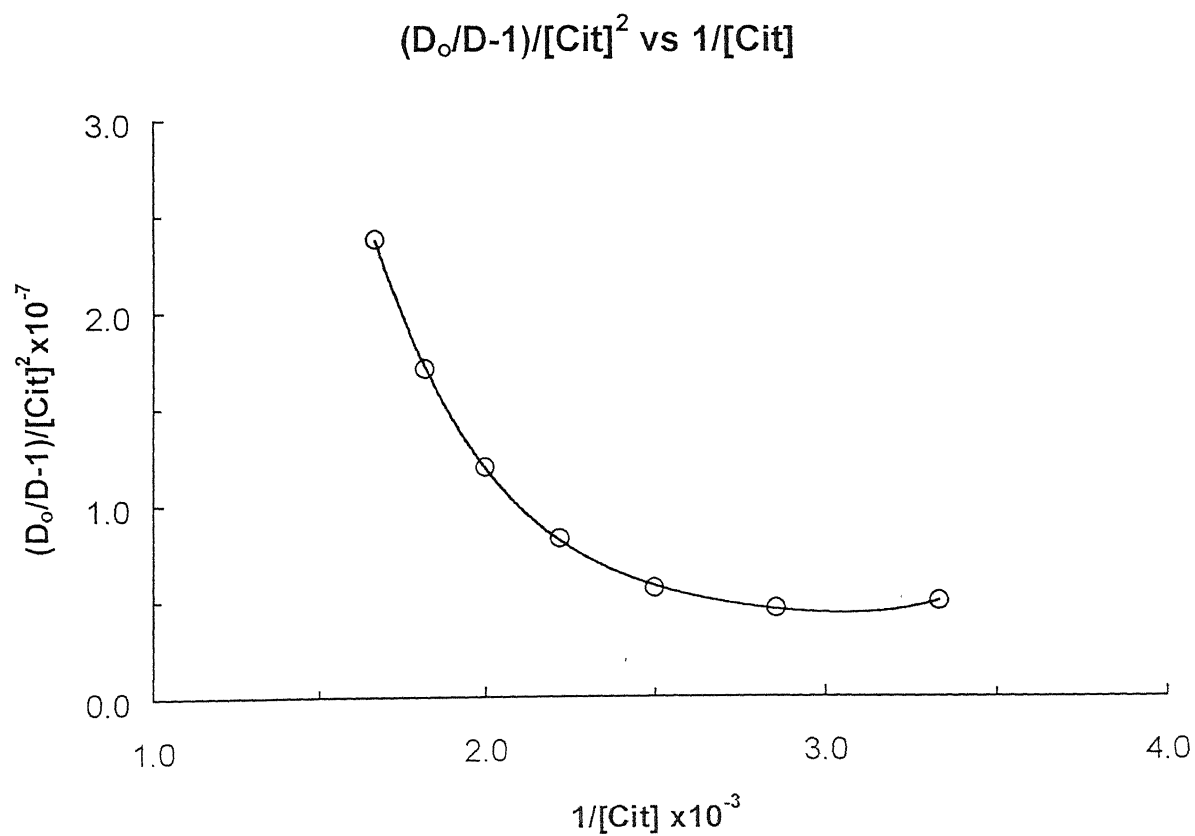
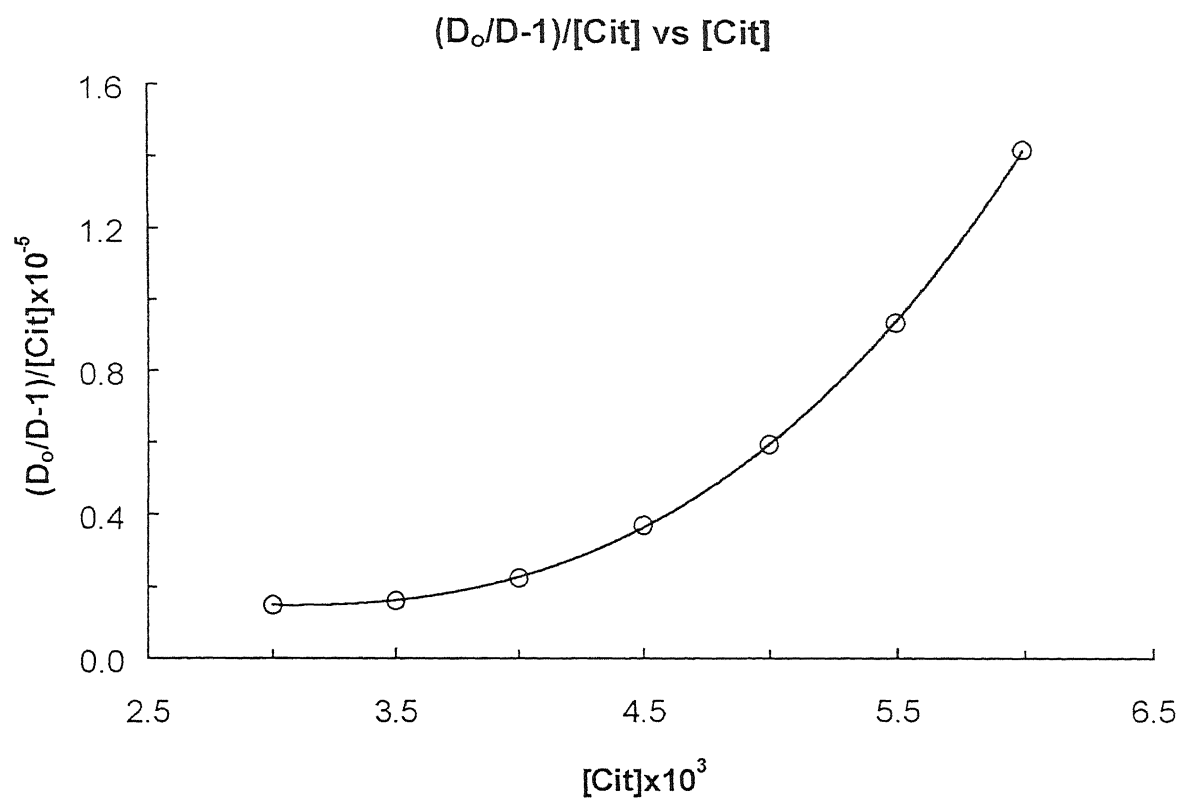


Fig. 4.11 Plot of Ni(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

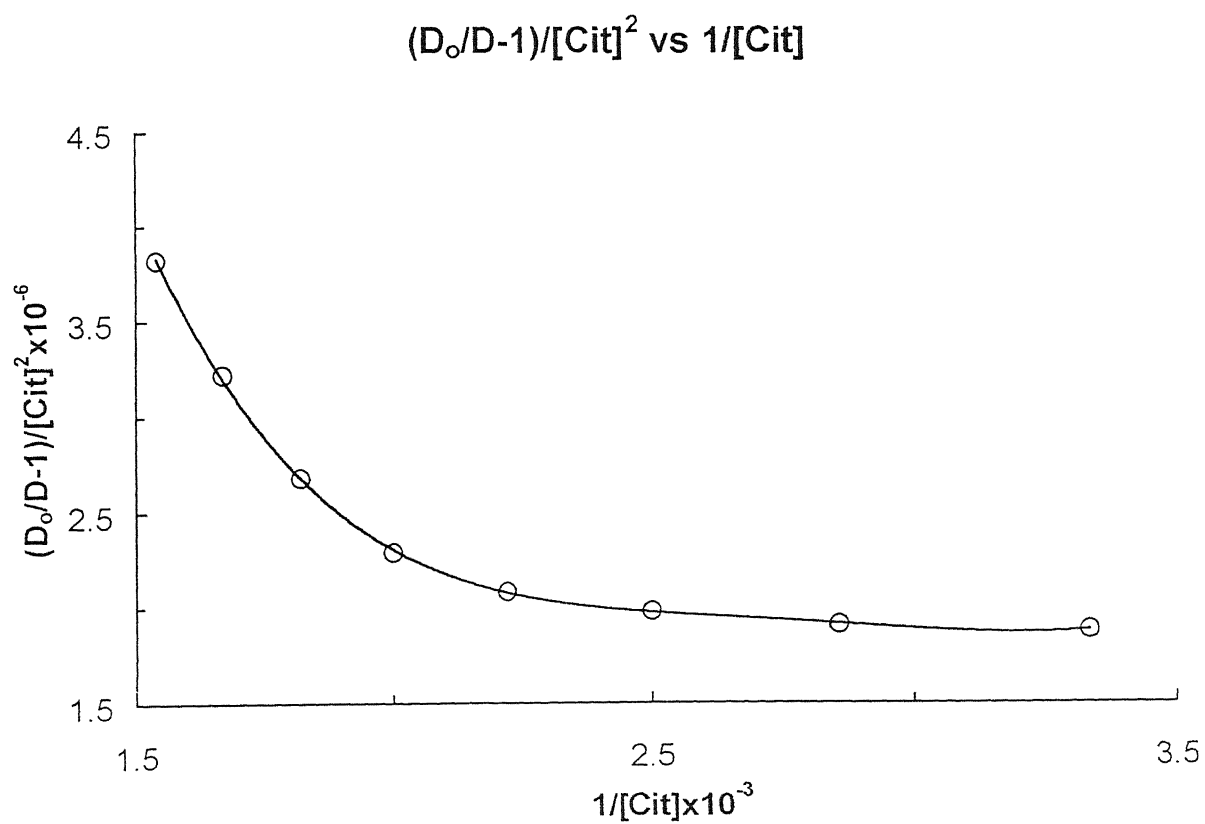
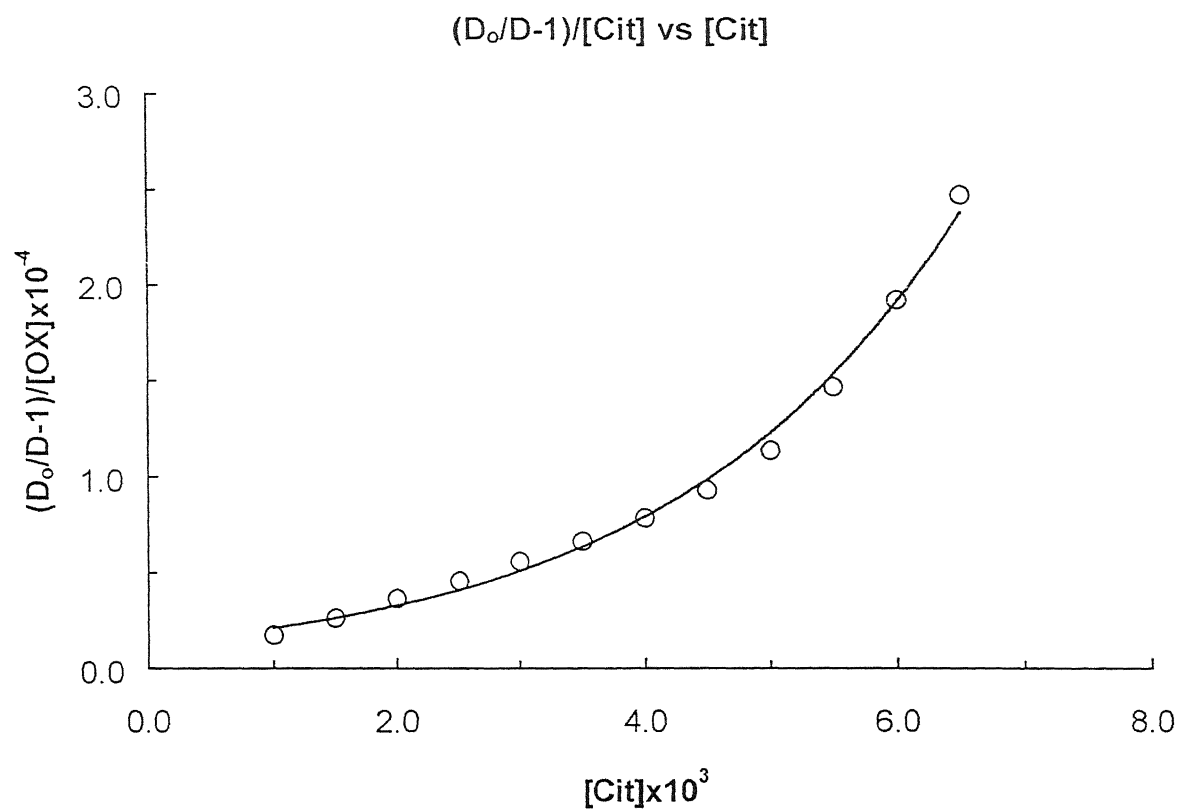


Fig. 4.12 Plot of Co(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

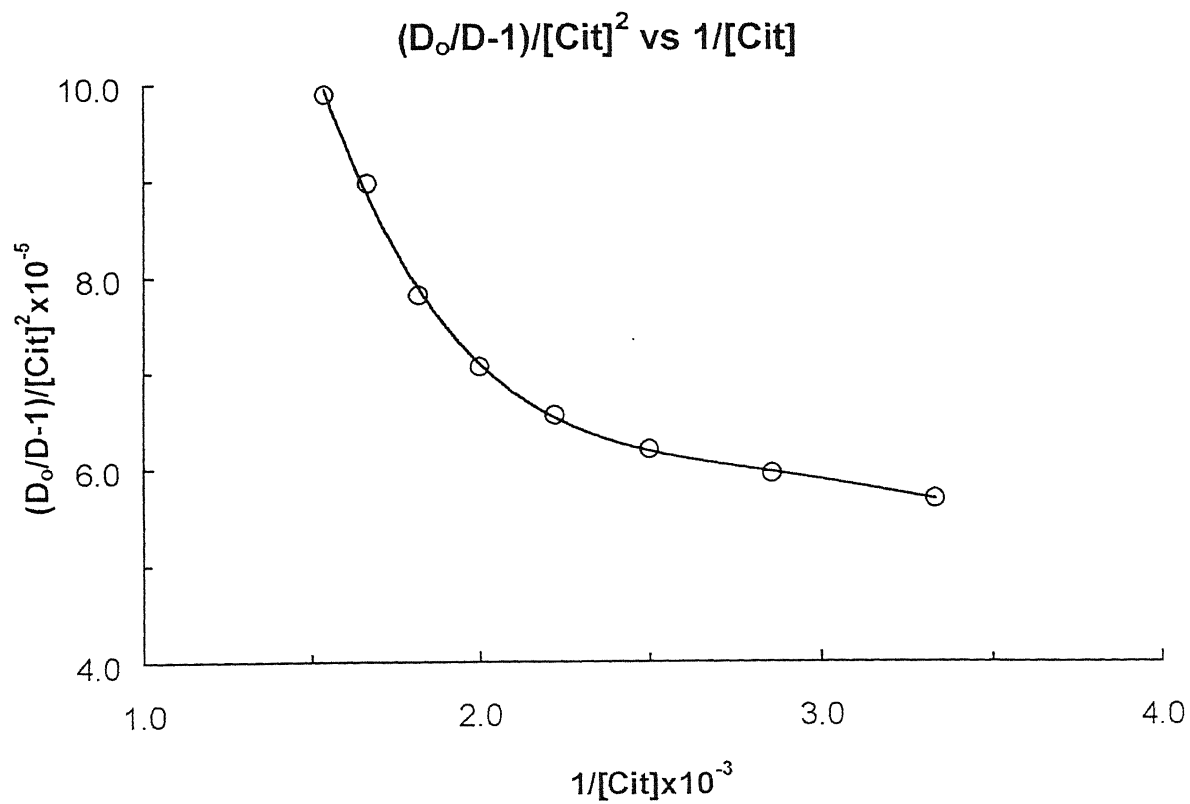
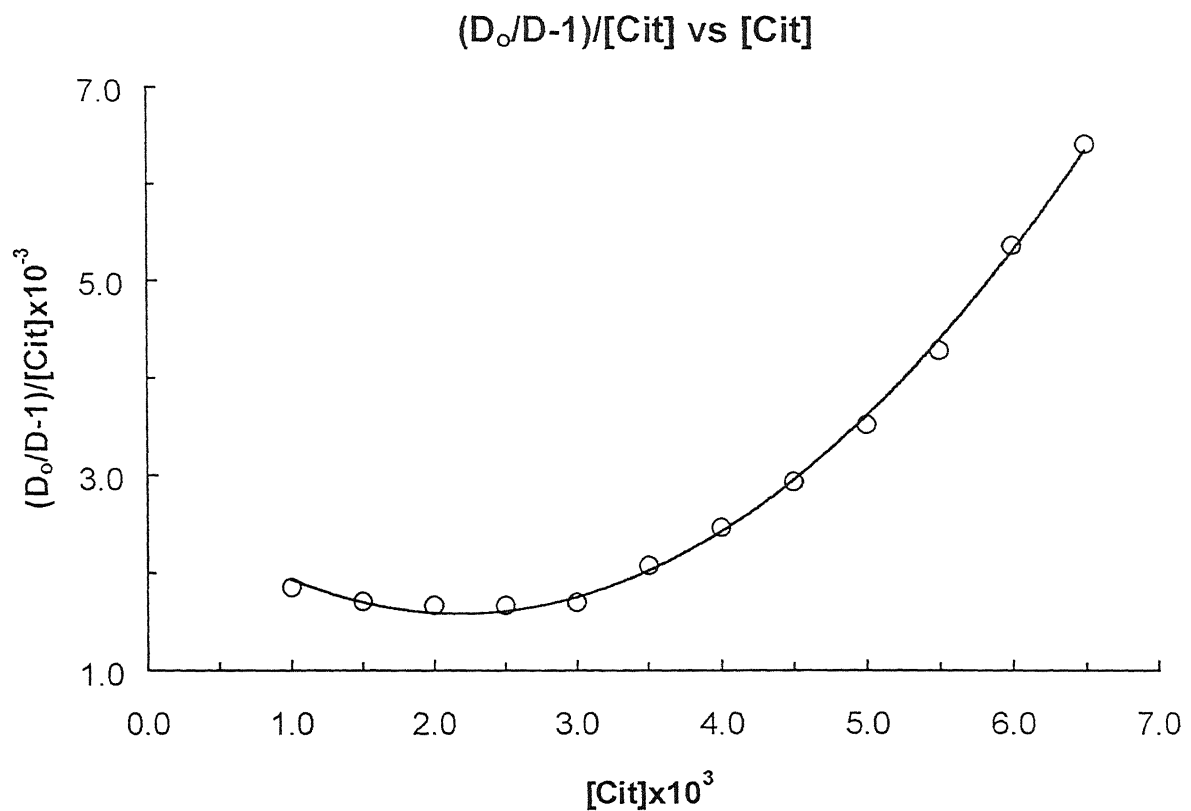
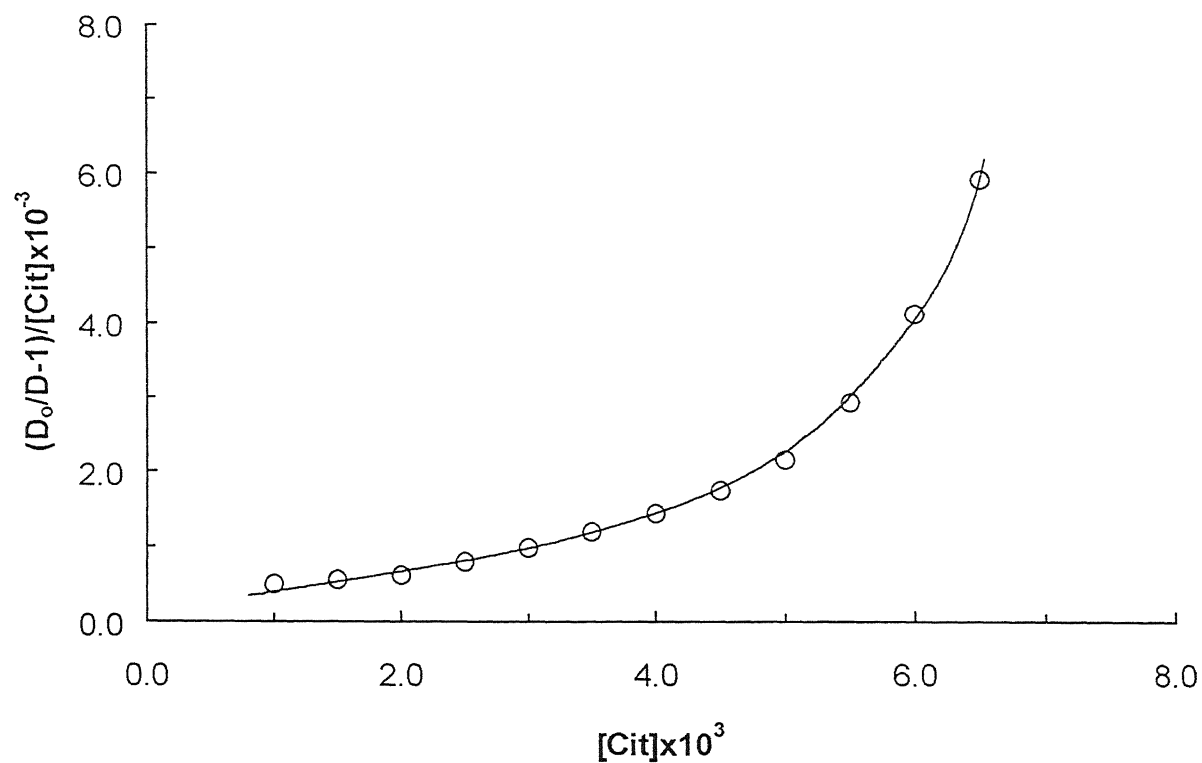


Fig. 4.13 Plot of Cu(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

$(D_o/D-1)/[\text{Cit}]$ vs $[\text{Cit}]$



$(D_o/D-1)/[\text{Cit}]^2$ vs $1/[\text{Cit}]$

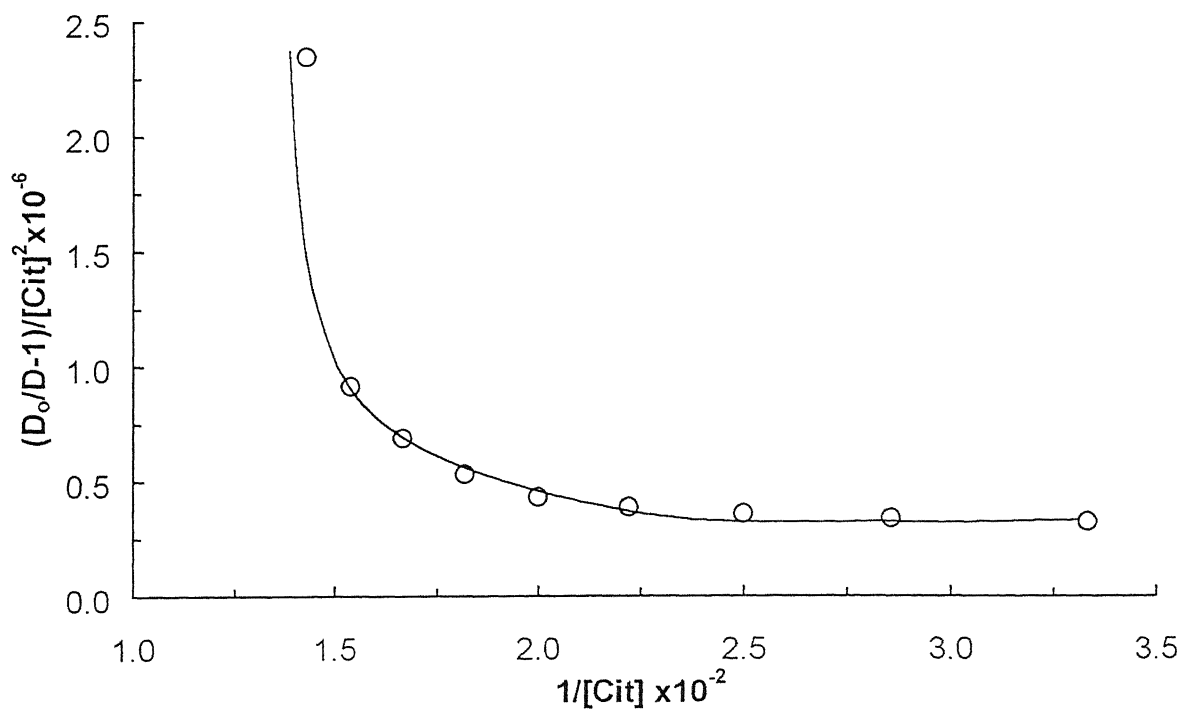


Fig. 4.14 Plot of Zn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

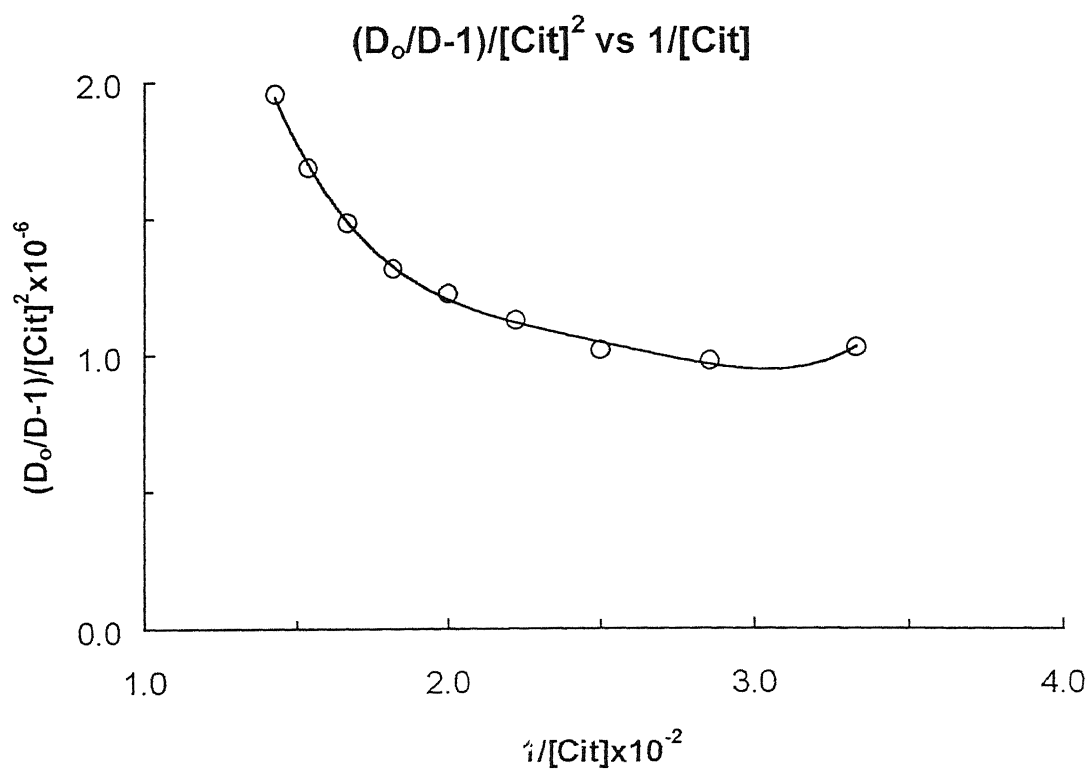
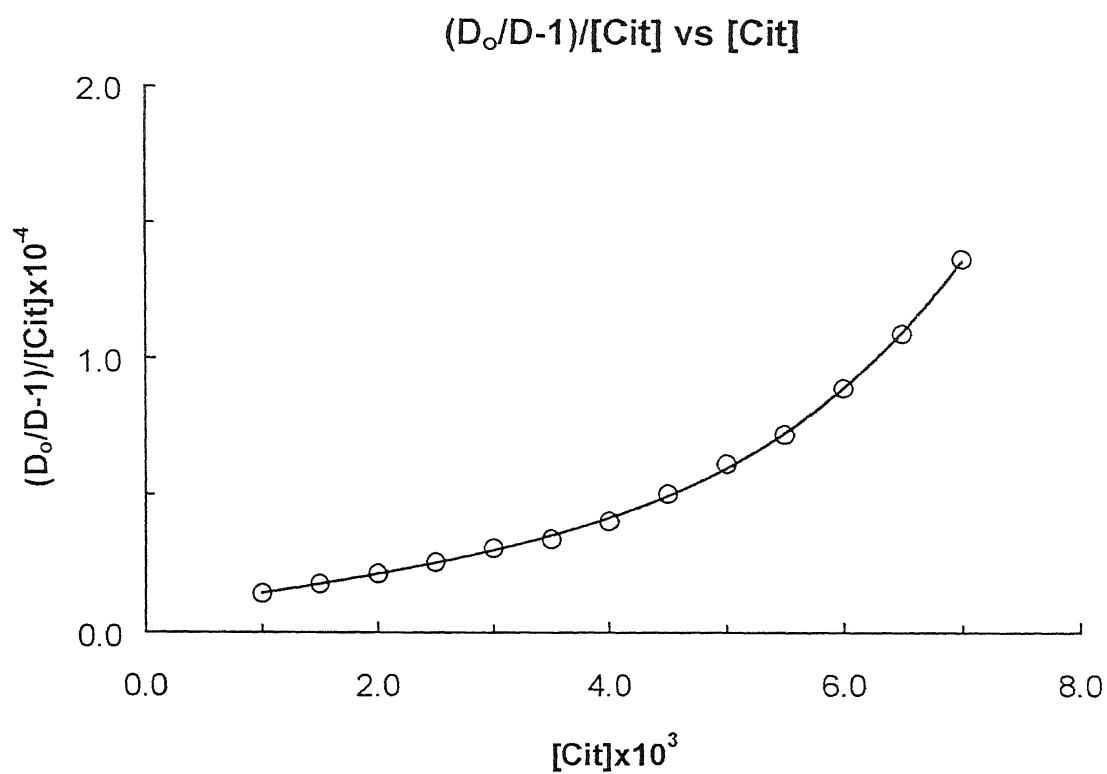
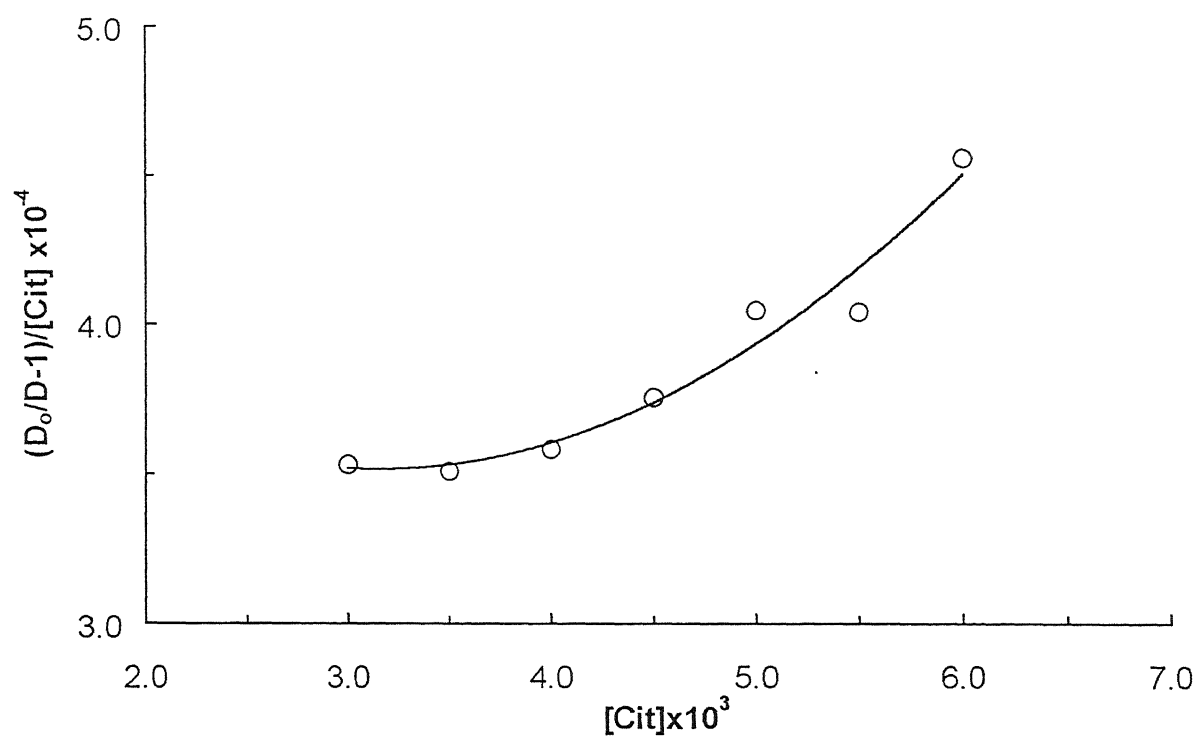


Fig. 4.15 Plot of Cd(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system
 $(D_0/D-1)/[\text{Cit}]$ vs $[\text{Cit}]$



$(D_0/D-1)/[\text{Cit}]^2$ vs $1/[\text{Cit}]$

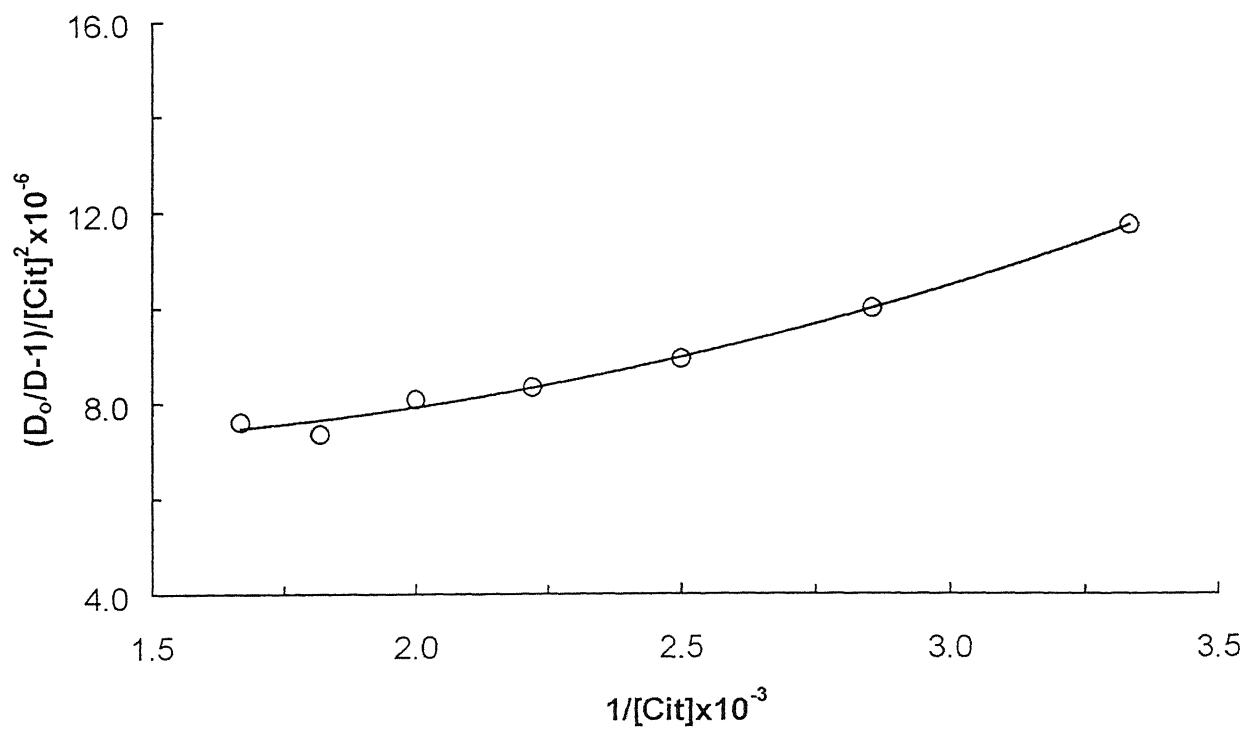


Fig. 4.16 Plot of Mg(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

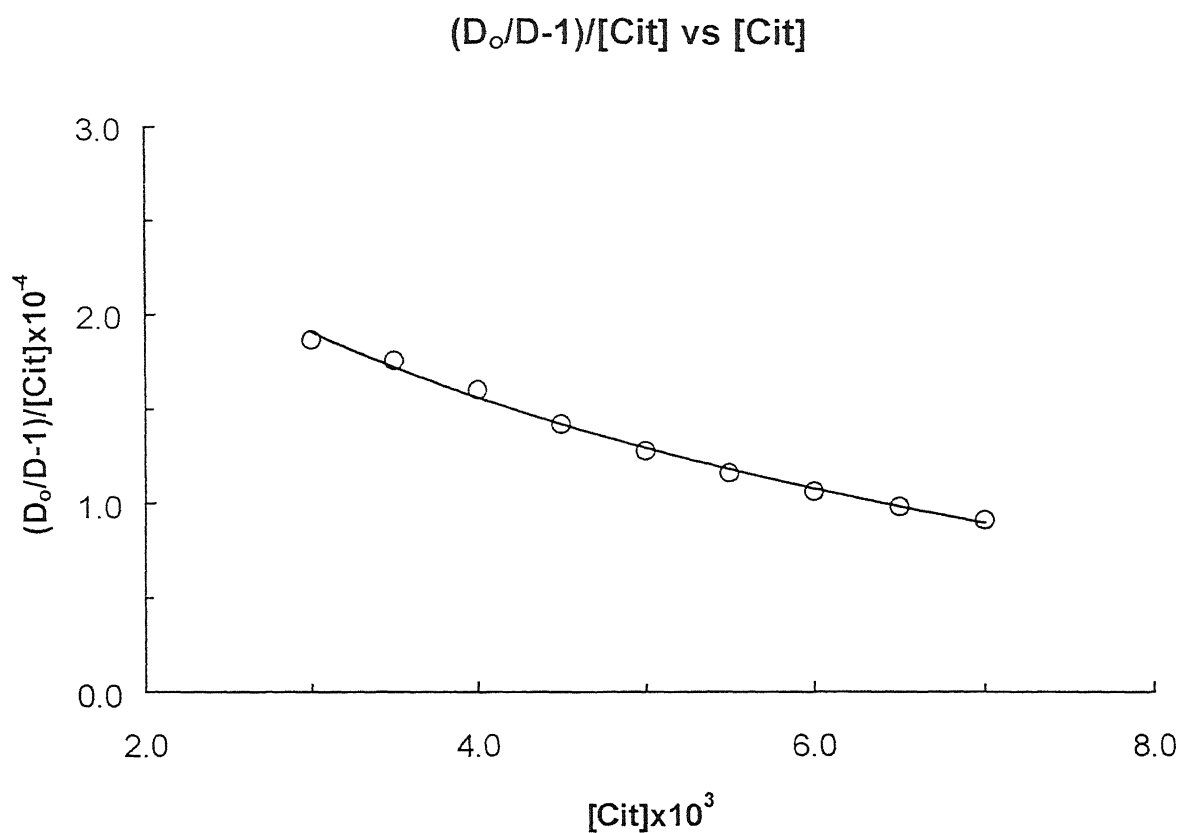


Fig. 4.17 Plot of Ca(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IR-120 system

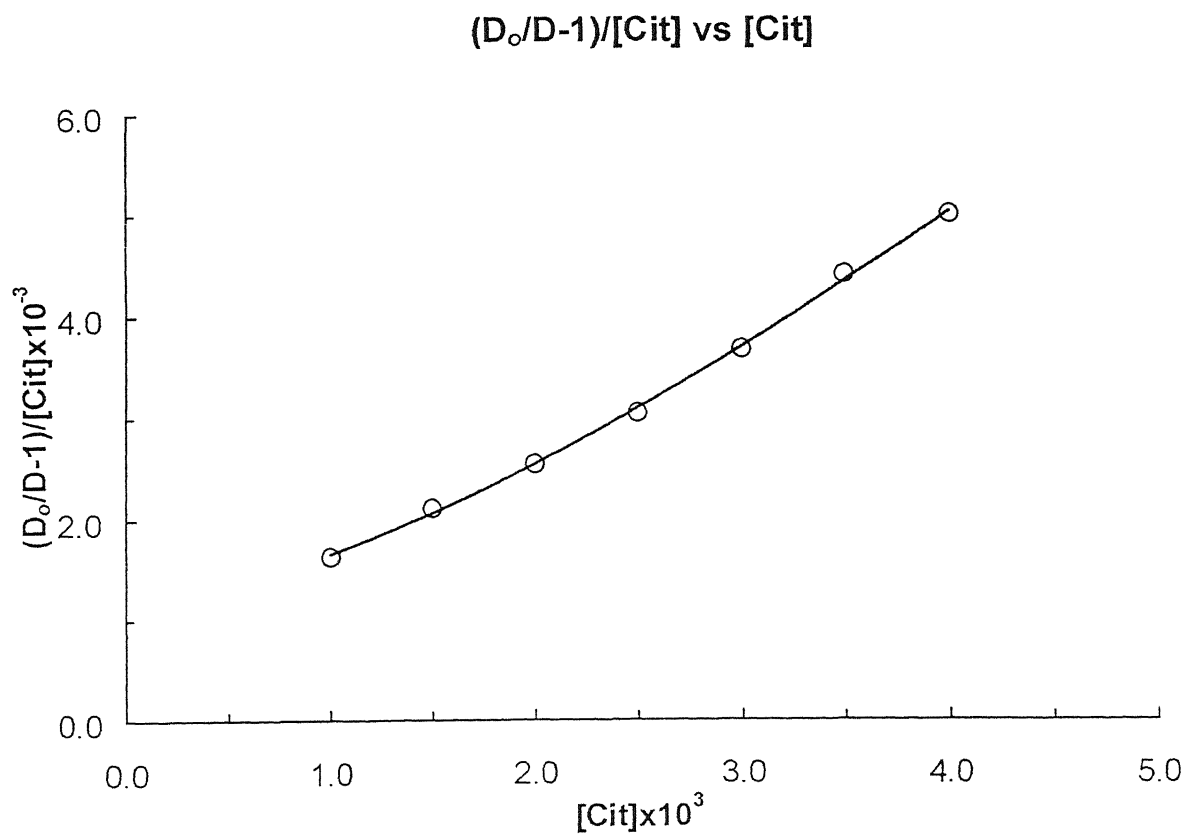
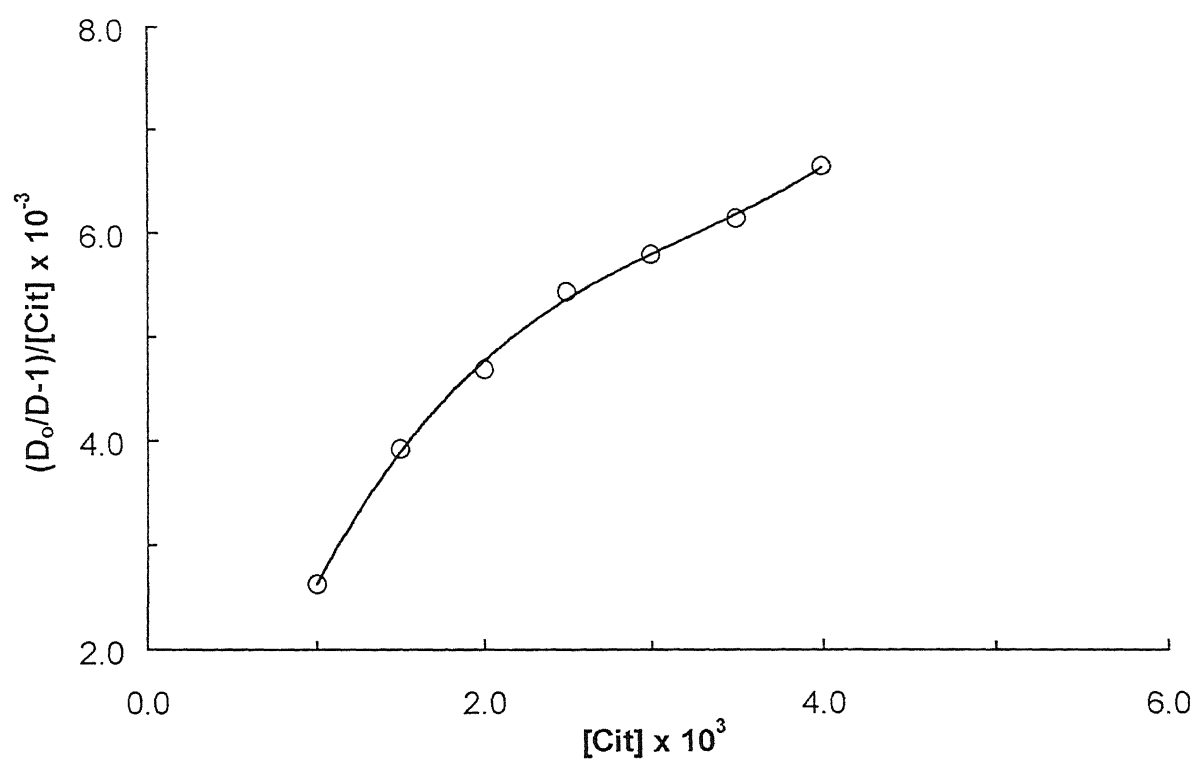


Fig. 4.18 Plot of Fe(II)-(NH₄)₃Cit(OH) Amberlite IR-120 system

$(D_0/D-1)/[Cit]$ vs $[Cit]$



The values of the various formation constants of the metal ions are tabulated along with the variable literature values Table 4.7. Though the formation of 1:2 (metal ligand) species has not been reported in the literature for metal ions, Mg(II), Ca(II), Mn(II), Fe(II), Ni(II), Co(II), and Cu(II), but in case of Fe(II), Zn(II) and Cd(II) anions exchange studies clearly indicate the formation of 1:1 as well as 1:2 anionic species as observed by their high sorption at higher ammonium citrate concentrations, Therefore, the second step formation constant is not unusual for these metal ions.

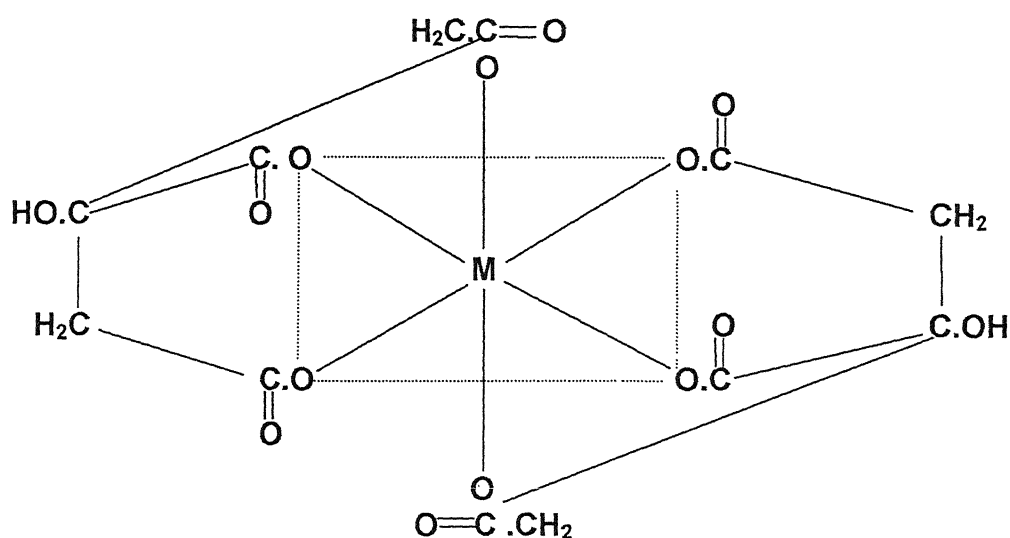
Table 4.7:- Values of formation constant obtained by Schubert's method

Metal Ion	D ₀	K ₁	LogK ₁	β ₂	logβ ₂
Mg(II)	5000.0	31923	4.50	-	-
Ca(II)	1056.2	3486	3.54	-	-
Mn(II)	769.2	12545	4.10	635579	5.80
Fe(II)	1191.2	7135.9	3.85	-	-
Fe(III)	1463.2	194630	5.29	212939285	8.33
Ni(II)	2500.0	27409	4.44	41992515	7.62
Co(II)	1428.5	2388.6	3.38	2318071	6.37
Cu(II)	1046.2	594163	5.77	7608051	6.88
Cu(II)	1046.2	594163	5.77	7608051	6.88
Zn(II)	694.3	79025	4.90	19539306	7.29
Cd(II)	6196.2	47324	4.68	8321423	6.92

The β₁ or K₁ values are comparable and the variation lies due to the basic nature of the metal ion species, and the ion exchange method where charge is effective or determining parameters. A large difference in case of Fe (III) K₁ and β₂ values cannot be explained by present results. Altogether the results are comparable with the literature findings, and the deviations may be contributed by the approach applied and the limitation of the technique which may not cover certain parameters due to the practical restrictions for performing the experiments. Definitely the ion exchange method is relatively based on the approach which is not so close like other techniques for determining the stability constant, but this method provides more practical values which are much more useful especially considering the problems like separations of species having quite close similar chemical nature. It is also important to note that the formation of second step stability constant is also established by

these investigations in case of Mn(II), Ni(II), Co(II), and Cu(II) which is not reported in literature or by any other worker. In these studies instead of citric acid the ammonium salt, i.e., $(\text{NH}_4)_3\text{Cit}(\text{OH})$ is used and probably in the absence of protonation the trivalent citrate anion is taking part in complexation with these metal ions and because of the poor competition by the NH_4^+ as compared to H^+ the metal citrate interactions are freely possible resulting to 1:2 species as well. The tentative structure may be assigned to 1:2 metal ligand complex species as an octahedron involving the complexation by three carboxylic acid groups (where OH at all is not taking part in complexation process).

Structure :-



The anion exchange investigations have also been performed like cation exchange studies, and the anion exchanger Amberlite IRA - 400 (in Cl^- - form) was used. The anion exchange sorption behaviour of each metal ion has shown in gradual increase with the corresponding increase in the concentration of

(NH_4)₃Cit(OH). The nature of sorption pattern is not varying much on comparing one metal by the other, but overall deviated sorption tendency of individual is closely linked with the complexation by the citrate, the anionic nature of the complex species from and the dissociation of the ammonium citrate (which is a salt of weak acid and weak base). It has been observed that Zn(II) shown continuous increase in the sorption with a highest distribution coefficient value equals to 1400 at a concentration of ammonium citrate = $7.0 \times 10^{-3} \text{M}$, while at the same concentration medium for Fe(III) the distribution coefficient value is = 5900, though their K_1 and β_2 value are $\text{Log } K_1 = 11.5(17)$ or $10.22(12)$ and $\text{log } \beta_2 = 15.94(12)$ for Fe(III) and $\text{log } K_1 = 4.98$ and $\text{log } \beta_2 = 10.88$ for Zn(II) respectively. The observed behavior is not following the possibility as per stability constant values, otherwise Fe^{3+} should have been shown more sorption in comparison to Zn (II), because of the more strong complexation of Fe (III) by the citrate. It is again indicating that in absence of or very poor protonation equilibrium, the trivalent citrate anion is definitely more strongly interacting with the Zn (II), resulting to more Zn (II) citrate anionic species consequently leading to its very high sorption even than with Fe(III). These investigation equilibria in solution and the ion exchange distribution equilibrium between the exchanger and the solution phases. Therefore, the ion exchange distribution effects are plain vital impacts with the complexation and dissociation equilibria effecting the normal complexation behaviour or the tendency of the metal ion involved. This may be an important difference responsible for the observed deviations in the formation constant values determined by ion exchange technique.

It is also interesting to note that Mg (II) and Ca (II) are p- block elements but their behaviour at lower citrate concentration is quite close to studied transition metal ions Ni (II), Fe (II), Co (II), Mn (II), Cu (II), Zn (II), Cd (II), and Fe (III), which is showing the degree of formation of the anionic species is of the same order and nature. It is also concluded that the affinity criteria of the individual metal ion anionic complex species is only slightly higher than the chloride anion resulting to the lower sorption, but as the concentration of anionic species gradually enhances the nature of anionic species definitely changes due to formation of higher anionic species except Mg (II) & Ca (II), therefore, the total amount of the anionic species as 1:1 and 1:2, enhances to more and more leading to higher sorption at higher concentration

ranges of ammonium citrate, of course the equilibrium has been reached for Mg(ii) at $4.0 \times 10^{-3} \text{M}$, $6.5 \times 10^{-3} \text{M}$ for Mn(II), 6.5×10^{-3} for Cu(II), 4.0×10^{-3} for Fe(II), $6.0 \times 10^{-3} \text{M}$ for Fe(III), $6.5 \times 10^{-3} \text{M}$ for Ni(II), $6.5 \times 10^{-3} \text{M}$ for Co(II), $4.0 \times 10^{-3} \text{M}$ for Ca(II), $5.0 \times 10^{-3} \text{M}$ for Cd(II). ammonium citrate concentration, which may be associated with the distribution equilibrium of Cl^- anion too.

Table 4.8:- Ni(II)– $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 (Cl^- form) system
treatment of the data by the modified method of Fronaeus

Cit $\times 10^3$	$\text{D}/[\text{Cit}]^2$ $\times 10^{-7}$	$\text{D}/[\text{Cit}]$ $\times 10^{-4}$	$\text{D}/\lambda_2[\text{Cit}]^2$ $\times 10^{-4}$	$1/[\text{Cit}]$ $\times 10^{-3}$	$1/[\text{Cit}]^2 - \beta_1 \lambda_1 / \text{D}$ $\times 10^{-3}$	$[\text{Cit}]/\text{D}$ $\times 10^{-5}$
1.0	1.11	1.11	1.71	1.00	3.55	9.00
1.5	0.89	1.33	1.37	0.67	2.08	7.50
2.0	0.83	1.65	1.27	0.50	1.35	6.05
2.5	0.80	2.00	1.23	0.40	0.96	5.00
3.0	0.79	2.37	1.21	0.33	0.73	4.22
3.5	0.79	2.78	1.22	0.29	0.57	3.60
4.0	0.82	3.27	1.26	0.25	0.46	3.06
4.5	0.85	3.84	1.31	0.22	0.38	2.61
5.0	0.93	4.67	1.44	0.20	0.32	2.14
5.5	1.09	5.97	1.67	0.18	0.26	1.67
6.0	1.33	7.98	2.05	0.17	0.22	1.25
6.5	1.54	10.00	2.37	0.15	0.19	1.00

Table 4.9:- Zn (II)– $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 (Cl^- form) system
treatment of the data by the modified method of Fronaeus

Cit $\times 10^3$	$\text{D}/[\text{Cit}]^2$ $\times 10^{-7}$	$\text{D}/[\text{Cit}]$ $\times 10^{-4}$	$\text{D}/\lambda_2[\text{Cit}]^2$ $\times 10^{-4}$	$1/[\text{Cit}]$ $\times 10^{-3}$	$1/[\text{Cit}]^2 - \beta_1 \lambda_1 / \text{D}$ $\times 10^{-5}$	$[\text{Cit}]/\text{D}$ $\times 10^{-5}$
1.0	3.64	3.64	2.60	1.00	0.46	2.75
1.5	2.76	4.14	1.97	0.67	0.27	2.41
2.0	1.91	3.82	1.37	0.50	0.22	2.62
2.5	1.71	4.28	1.22	0.40	0.16	2.34
3.0	1.33	3.99	0.95	0.33	0.14	2.51
3.5	1.34	4.70	0.96	0.29	0.10	2.13
4.0	1.39	5.54	0.99	0.25	0.08	1.80
4.5	1.41	6.36	1.01	0.22	0.06	1.57
5.0	1.53	7.63	1.09	0.20	0.05	1.31
5.5	1.65	9.09	1.18	0.18	0.03	1.10
6.0	1.81	10.83	1.29	0.17	0.03	0.92
6.5	2.13	13.85	1.52	0.15	0.02	0.72
7.0	2.86	20.00	2.04	0.14	0.01	0.50

Table-4.10: Mn(II)–(NH₄)₃Cit(OH) Amberlite IRA-400 (Cl[–]- form) system

treatment of the data by the modified method of Fronaeus

Cit x10 ³	D/[Cit] ² x10 ^{–7}	D/[Cit] x10 ^{–4}	D/λ ₂ [Cit] ² x10 ^{–4}	1/[Cit] x10 ^{–3}	1/[Cit] ² –β ₁ λ ₁ /D x10 ^{–5}	[Cit]/D x10 ^{–5}
1.0	25.00	2.50	7.61	1.00	-13.64	4.00
1.5	14.81	2.22	4.51	0.67	-11.06	4.50
2.0	10.71	2.14	3.26	0.50	-8.79	4.67
2.5	9.26	2.32	2.82	0.40	-6.21	4.32
3.0	8.50	2.55	2.59	0.33	-4.39	3.92
3.5	7.64	2.67	2.32	0.29	-3.46	3.74
4.0	7.14	2.86	2.17	0.25	-2.67	3.50
4.5	6.91	3.11	2.10	0.22	-2.00	3.21
5.0	6.91	3.45	2.10	0.20	-1.42	2.89
5.5	6.61	3.64	2.01	0.18	-1.14	2.75
6.0	6.48	3.89	1.97	0.17	-0.87	2.57
6.5	7.78	5.05	2.37	0.15	-0.26	1.98
7.0	6.71	4.69	2.04	0.14	-0.37	2.13

Table-4.11: Co(II)–(NH₄)₃Cit(OH) Amberlite IRA-400 (Cl[–]-form) system

treatment of the data by the modified method of Fronaeus

Cit x10 ³	D/[Cit] ² x10 ^{–7}	D/[Cit] x10 ^{–4}	D/λ ₂ [Cit] ² x10 ^{–4}	1/[Cit] x10 ^{–3}	1/[Cit] ² –β ₁ λ ₁ /D x10 ^{–2}	[Cit]/D x10 ^{–5}
1.0	20.00	2.00	6.67	1.00	9.35	5.00
1.5	11.11	1.67	3.70	0.67	6.14	6.00
2.0	7.61	1.52	2.54	0.50	4.57	6.57
2.5	5.82	1.45	1.94	0.40	3.64	6.88
3.0	4.76	1.43	1.59	0.33	3.03	7.00
3.5	4.73	1.65	1.58	0.29	2.63	6.05
4.0	4.78	1.91	1.59	0.25	2.33	5.24
4.5	4.94	2.22	1.65	0.22	2.09	4.50
5.0	5.23	2.62	1.74	0.20	1.90	3.82
5.5	5.71	3.14	1.90	0.18	1.74	3.18
6.0	6.48	3.89	2.16	0.17	1.61	2.57
6.5	7.10	4.62	2.37	0.15	1.49	2.17
7.0	6.12	4.29	2.04	0.14	1.39	2.33

Table 4.12:- Cu(II)–(NH₄)₃Cit(OH) Amberlite IRA-400 (Cl[–]-form) system
treatment of the data by the modified method of Fronaeus

Cit x10 ³	D/[Cit] ² x10 ^{–7}	D/[Cit] x10 ^{–4}	D/λ ₂ [Cit] ² x10 ^{–4}	1/[Cit] x10 ^{–3}	1/[Cit] ² –β ₁ λ ₁ /D x10 ^{–2}	[Cit]/D x10 ^{–5}
1.0	11.11	1.11	2.92	1.00	-157.45	9.00
1.5	7.84	1.18	2.06	0.67	-98.80	8.50
2.0	6.25	1.25	1.64	0.50	-69.42	8.00
2.5	5.33	1.33	1.40	0.40	-51.82	7.50
3.0	4.13	1.24	1.09	0.33	-46.68	8.06
3.5	3.77	1.32	0.99	0.29	-37.41	7.58
4.0	3.51	1.40	0.92	0.25	-30.63	7.12
4.5	3.72	1.67	0.98	0.22	-22.47	5.97
5.0	4.02	2.01	1.06	0.20	-16.49	4.97
5.5	4.89	2.69	1.29	0.18	-10.76	3.72
6.0	6.28	3.77	1.65	0.17	-6.56	2.65
6.5	8.99	5.85	2.37	0.15	-3.36	1.71
7.0	7.76	5.43	2.04	0.14	-3.47	1.84

Table 4.13:- Cd (II)–(NH₄)₃Cit(OH) Amberlite IRA-400 (Cl[–]-form) system
treatment of the data by the modified method of Fronaeus

Cit x10 ³	D/[Cit] ² x10 ^{–7}	D/[Cit] x10 ^{–4}	D/λ ₂ [Cit] ² x10 ^{–4}	1/[Cit] x10 ^{–3}	1/[Cit] ² –β ₁ λ ₁ /D x10 ^{–2}	[Cit]/D x10 ^{–5}
1.0	11.11	1.11	2.22	1.00	-157.45	9.00
1.5	14.81	2.22	2.96	0.67	-98.80	8.50
2.0	16.67	3.33	3.33	0.50	-69.42	8.00
2.5	17.10	4.28	3.42	0.40	-51.82	7.50
3.0	19.19	5.76	3.84	0.33	-46.68	8.06
3.5	17.69	6.19	3.54	0.29	-37.41	7.58
4.0	17.19	6.88	3.44	0.25	-30.63	7.12
4.5	16.20	7.29	3.24	0.22	-22.47	5.97
5.0	16.00	8.00	3.20	0.20	-16.49	4.97
5.5	15.95	8.77	3.19	0.18	-10.76	3.72
6.0	13.89	8.33	2.78	0.17	-6.56	2.65
6.5	11.83	7.69	2.37	0.15	-3.36	1.71
7.0	10.20	7.14	2.04	0.14	-3.47	1.84

Table 4.14:- The data by the modified method of Fronaeus for Amberlite IRA-400 (Cl⁻ form) system treatment

Ca (II)–(NH ₄) ₃ Cit(OH)				Mg (II)–(NH ₄) ₃ Cit(OH)			
Cit x10 ³	D/[Cit] x10 ⁻⁴	1/[Cit] ² –β ₁ λ ₁ /D x10 ⁻²	[Cit]/D x10 ⁻⁵	Cit x10 ³	D/[Cit] x10 ⁻⁴	1/[Cit] ² –β ₁ λ ₁ /D x10 ⁻²	[Cit]/D x10 ⁻⁵
1.0	2.50	-2.87	4.00	1.0	3.64	-6.09	2.75
1.5	2.64	-1.47	3.79	1.5	3.86	-3.44	2.59
2.0	2.89	-0.56	3.45	2.0	4.38	-1.69	2.29
2.5	3.27	0.07	3.06	2.5	4.00	-1.85	2.55
3.0	3.81	0.52	2.63	3.0	3.81	-1.79	2.39
3.5	4.60	0.86	2.18	3.5	3.49	-1.93	2.86
4.0	5.00	0.89	2.00	4.0	3.27	-1.98	3.06
4.5	4.44	0.61	2.25	4.5	2.91	-2.25	3.44
5.0	4.00	0.39	2.50	5.0	2.62	-2.48	3.82
5.5	3.64	0.21	2.75	5.5	2.38	-2.66	4.21
6.0	3.33	0.06	3.00	6.0	2.18	-2.81	4.59
6.5	3.08	-0.07	3.25	6.5	2.01	-2.94	4.97
7.0	2.86	-0.18	3.50	7.0	1.87	-3.05	5.35

Fe (II)–(NH ₄) ₃ Cit(OH)			
Cit x10 ³	D/[Cit] x10 ⁻⁴	1/[Cit] ² –β ₁ λ ₁ /D x10 ⁻²	[Cit]/D x10 ⁻⁵
1.0	3.04	8.93	3.29
1.5	3.86	6.11	2.59
2.0	4.25	4.62	2.35
2.5	4.57	3.72	2.19
3.0	5.00	3.12	2.00
3.5	5.20	2.68	1.92
4.0	5.25	2.35	1.90
4.5	5.38	2.09	1.86
5.0	4.67	1.86	2.14
5.5	4.24	1.68	2.36
6.0	3.89	1.53	2.57
6.5	3.59	1.40	2.79
7.0	3.33	1.29	3.00

The citrate anion with three negative charges is definitely taking part in the exchange process and competing with the complexed anionic species, but as per general ion exchange sorption rule high molecular weight species are relatively more preferred by the exchanger therefore, metal citrate complex should be preferred much more than the citrate itself, as has been observed in present studied.

The anion exchanger data have also been used to work out the metal citrate complexation equilibrium constants. The stability constants have been evaluated using the treatment of Fronaeus approach (chapter-2). The complexation equilibria in solution may be given as described for the cation exchange systems. The overall gross metal ions distribution with an anion exchanger for a metal ligand systems having species upto ML_2 may be given as,

$$D = [ML][ML_2] / [M][ML][ML_2]$$

Taking into account the distribution of individual species according to eq.(6) (chapter-2) then

$$D = \lambda_1 K_1 [L] + \lambda_2 \beta_2 [L]^2 / 1 + K_1 [L] + \beta_2 [L]^2 \quad \text{————— (5)}$$

Where λ_1 and λ_2 indicates the distribution coefficient of ML and ML_2 species, respectively,

$$\text{Or} \quad D / \lambda_2 [L]^2 = \lambda_1 \beta_1 / \lambda_2 [L] + \beta_2 - D.F / \lambda_2 [L] \quad \text{————— (6)}$$

$$(F = K_1 [L] + \beta_2 [L]^2)$$

$$\text{Or} \quad D/[L] = \lambda_1 \beta_1 + \lambda_2 \beta_2 [L] - D.F / \lambda_2 [L] \quad \text{————— (7)}$$

$$\text{Or} \quad 1/[L] = \lambda_1 \beta_1 + \lambda_2 \beta_2 [L]/D - (K_1 [L] + \beta_2 [L]^2) / [L] \quad \text{—— (8)}$$

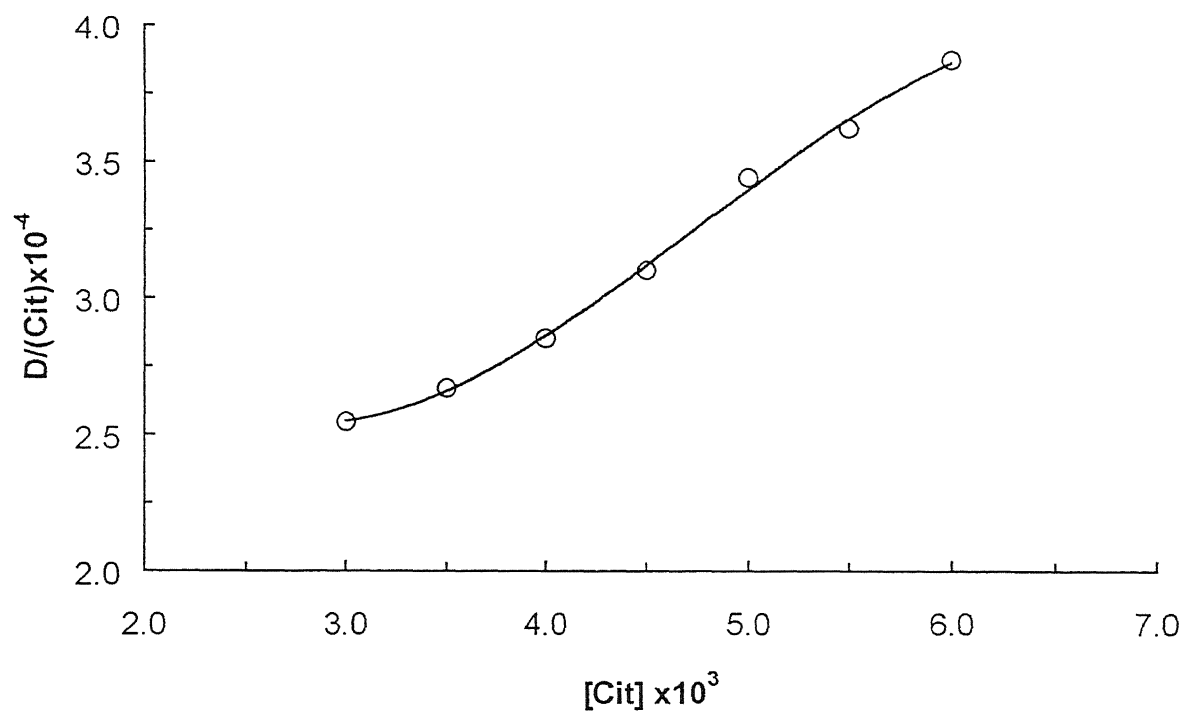
and from equations (6 and 7) on extrapolating the curves $D/[L]^2$ vs $1/[L]$ and $D/[L]$ Vs $[L]$ to zero $[L]$ concentration β_2 is obtained as the limiting values at the intercept of the respective plots. Rearranging equation (8) then,

$$(1/[L] - \beta_1 \lambda_1 / D) = \lambda_2 \beta_2 [L] / D - K_1 + \beta_2 [L]$$

The plot of $(1/[L] - \beta_1 \lambda_1 / D)$ Vs $[L] / D$ to zero $[L]$ concentration gives K_1 as limiting value of the intercept. (Fig 4.19a, 4.19b, 4.20a, 4.20b, 4.21a, 4.21b, 4.22a, 4.22b, 4.23a, 4.23b, 4.24a, 4.24b, 4.25a, 4.25b, 4.26, 4.27, 4.28) . The various experimental parameters and the calculated quantities are summarized in Table 4.8, 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, .

Fig. 4.19.a Plot of Mn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

$D/[\text{Cit}]$ vs $[\text{Cit}]$



$1/([\text{Cit}] - \beta_1 \lambda_1 / D)$ vs $[\text{Cit}] / D$

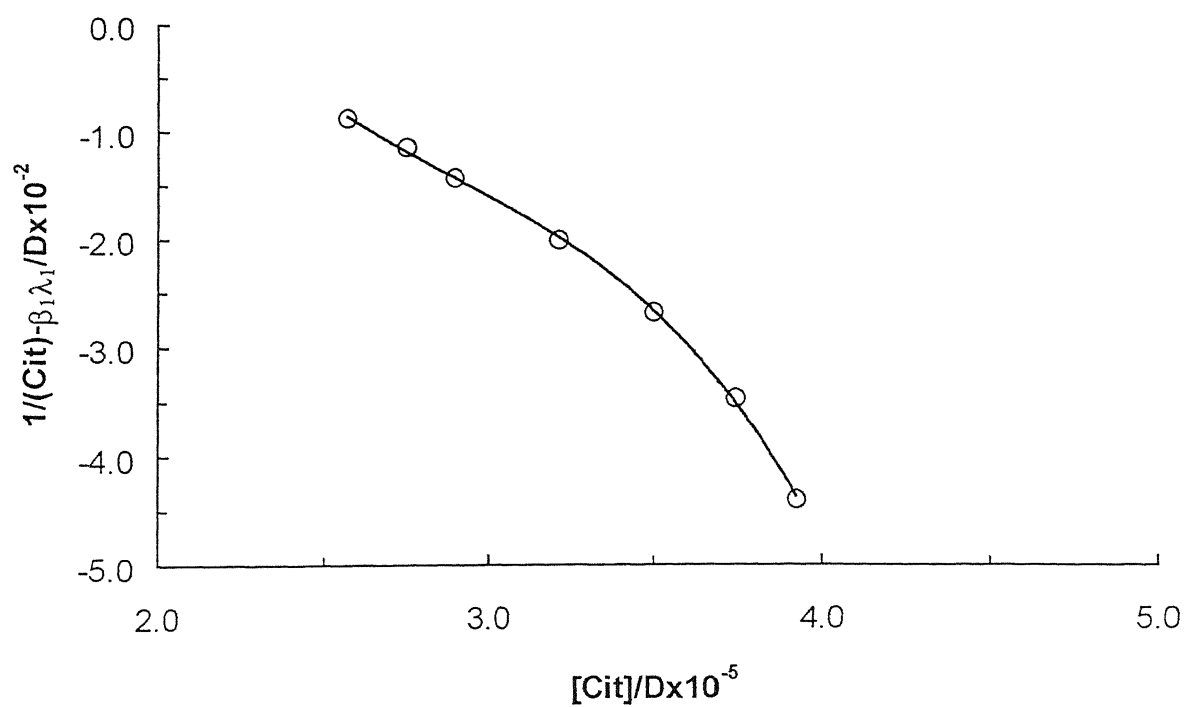


Fig. 4.19.b Plot of Mn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

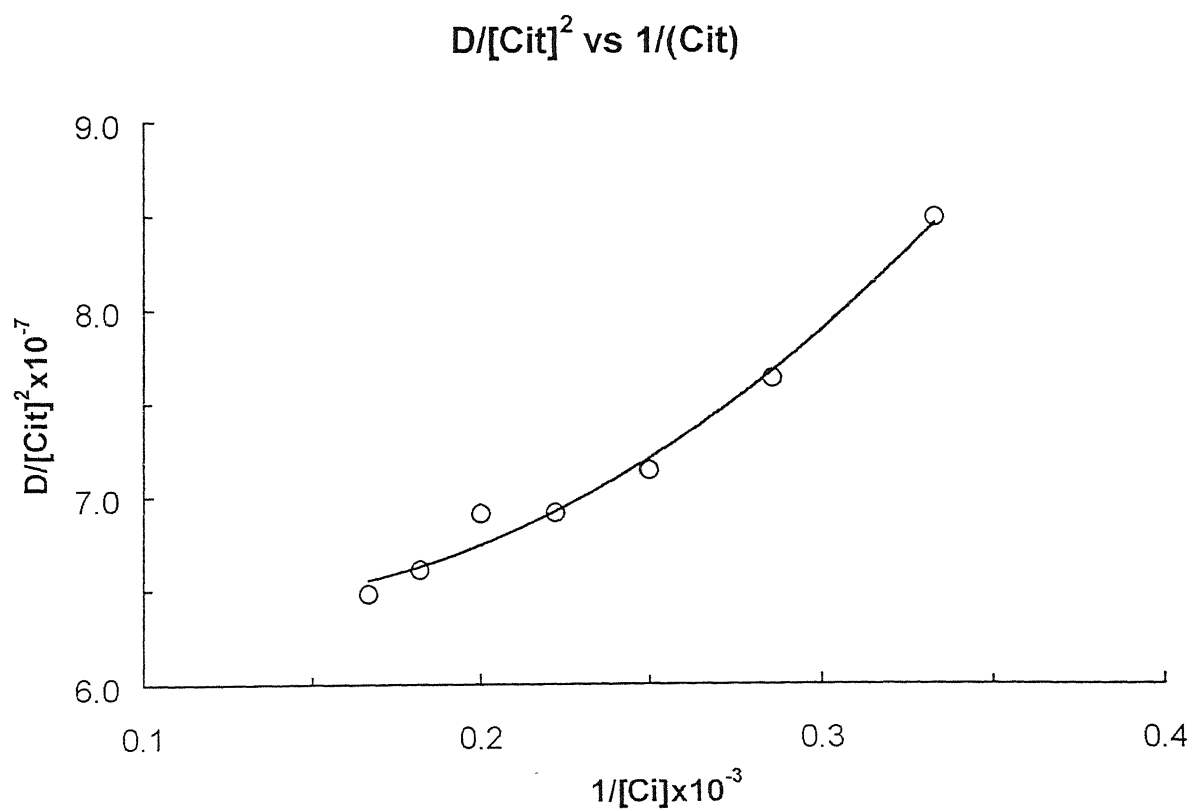
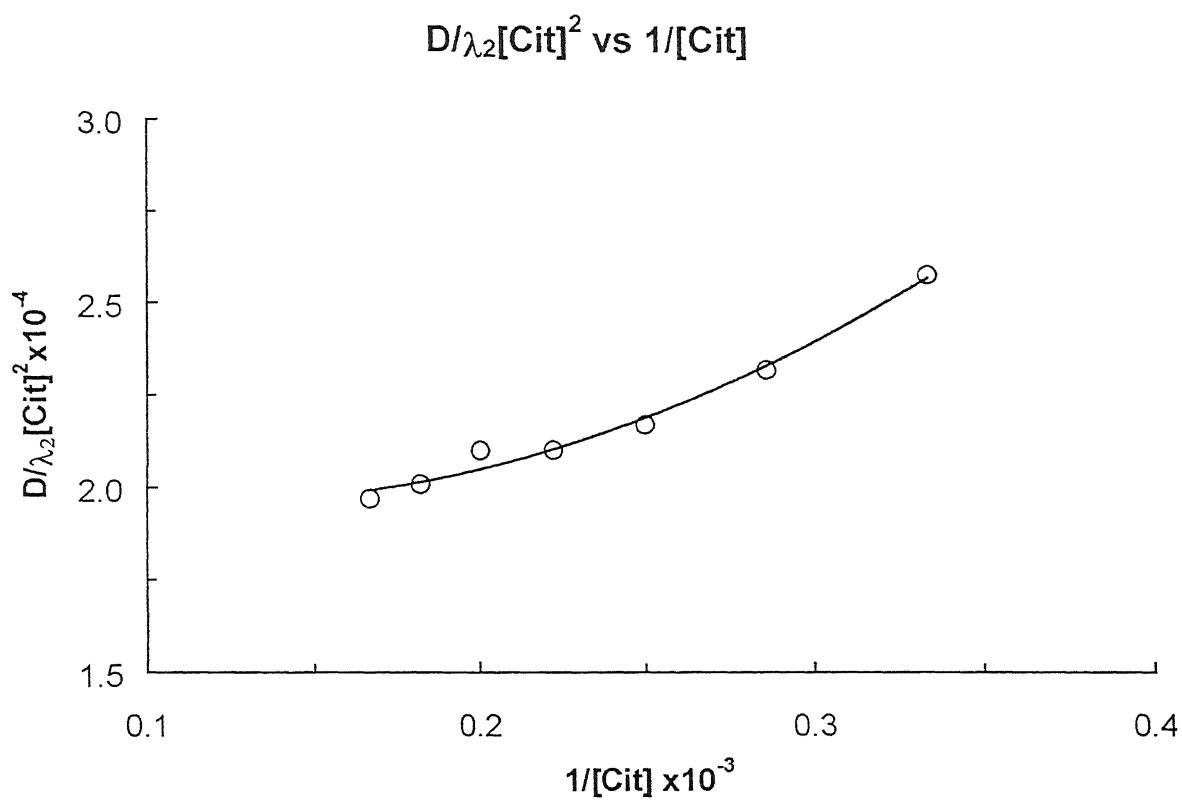
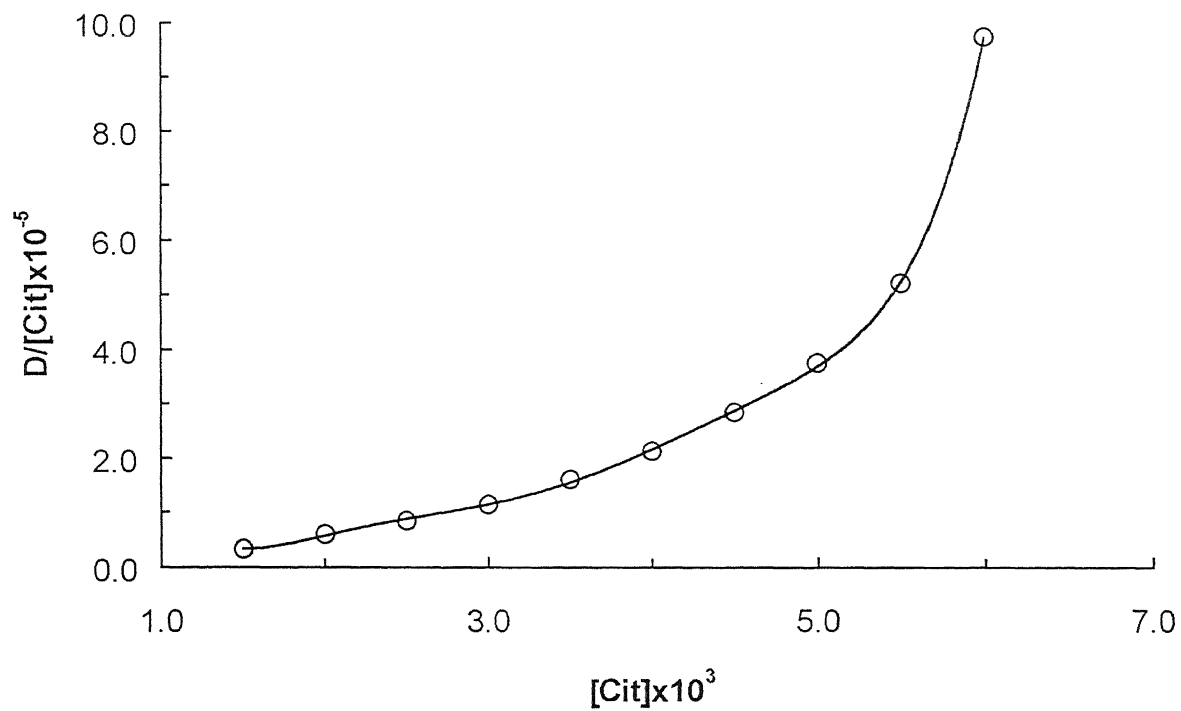


Fig. 4.20.a Plot of Fe(III)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

D/[Cit] vs [Cit]



$1/[Cit] - \beta_1 \lambda_1 / D$ vs $[Cit]/D$

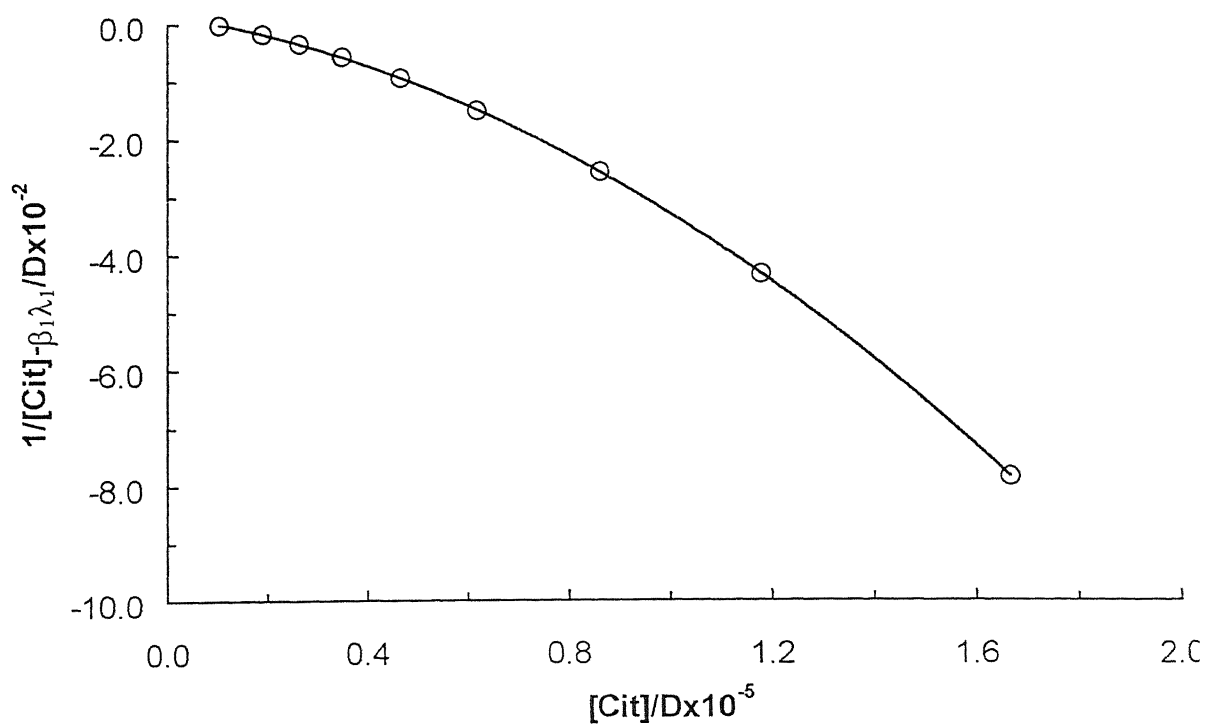


Fig. 4.20.b Plot of Fe(III)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

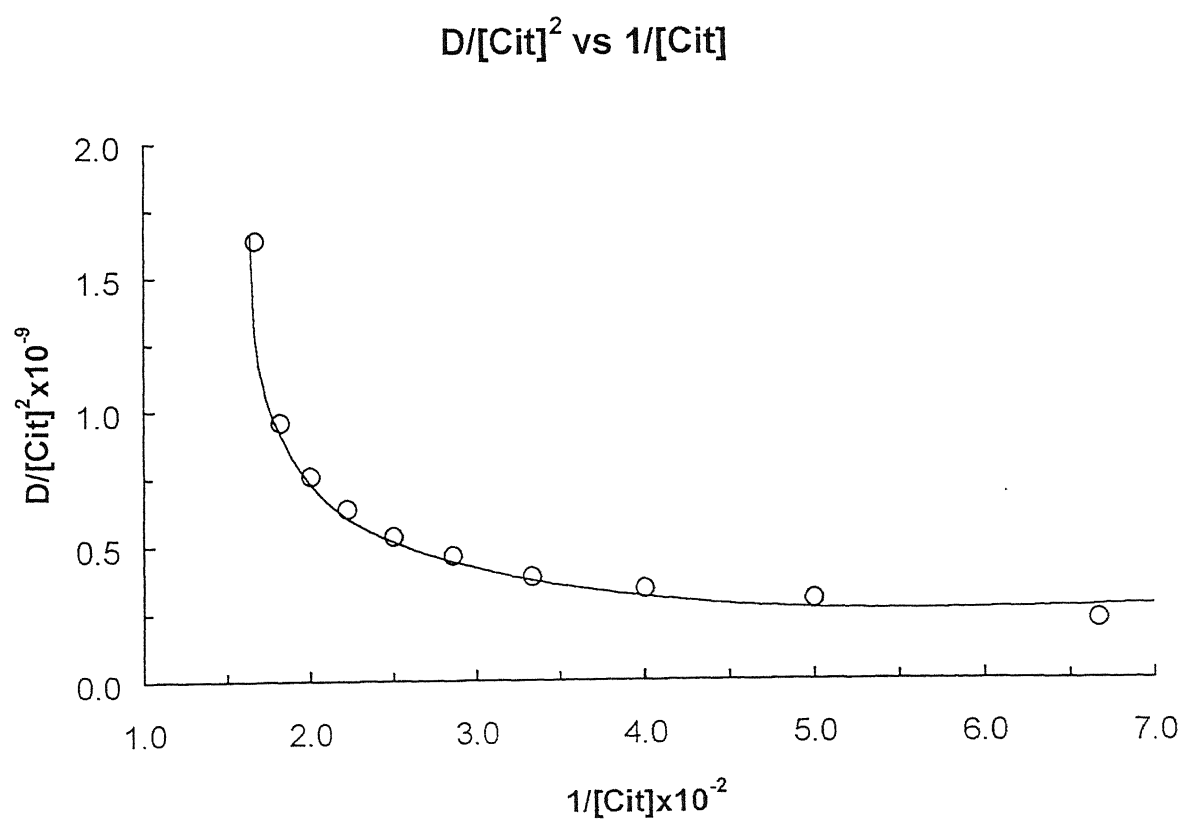
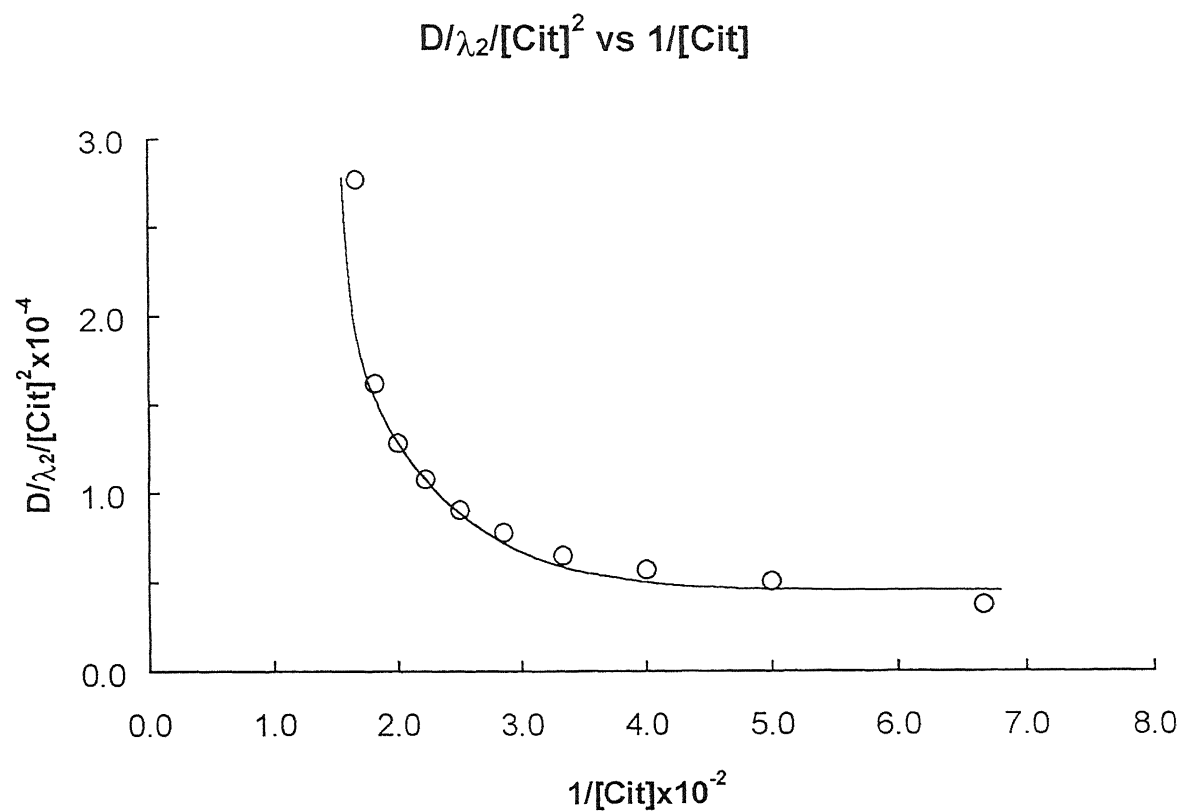
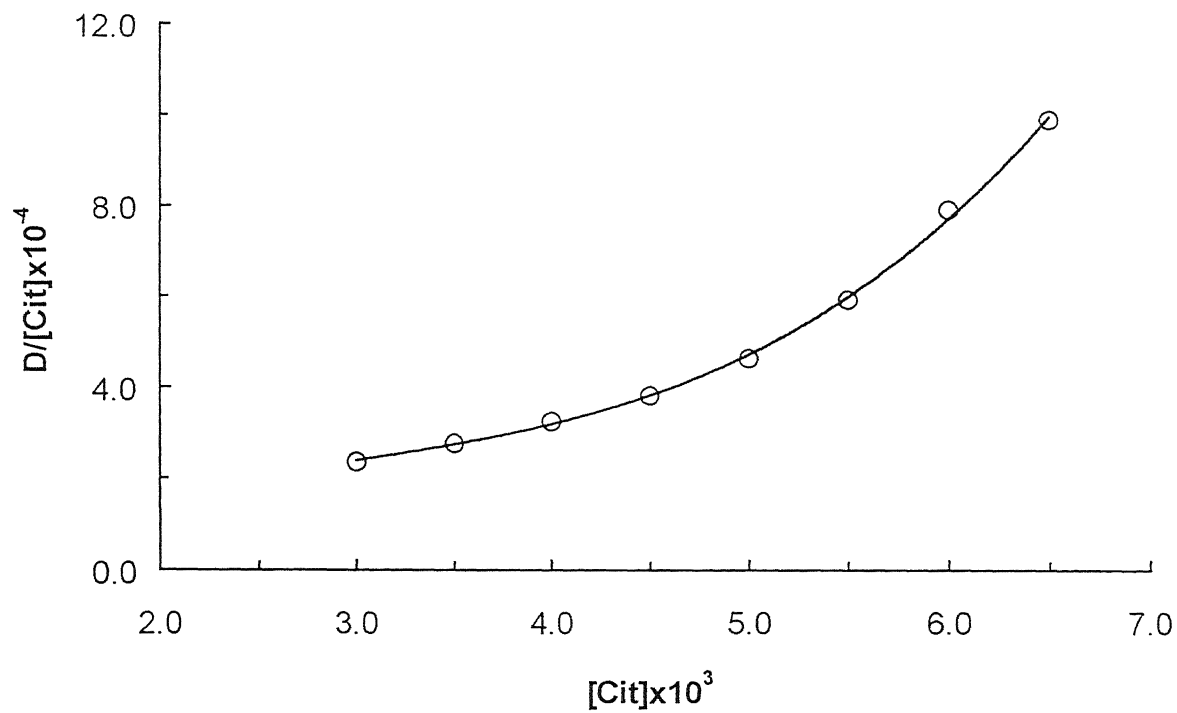


Fig. 4.21.a Plot of Ni(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

$D/[\text{Cit}]$ vs $[\text{Cit}]$



$1/[\text{Cit}] - \beta_1 \lambda_1 / D$ vs $[\text{Cit}] / D$

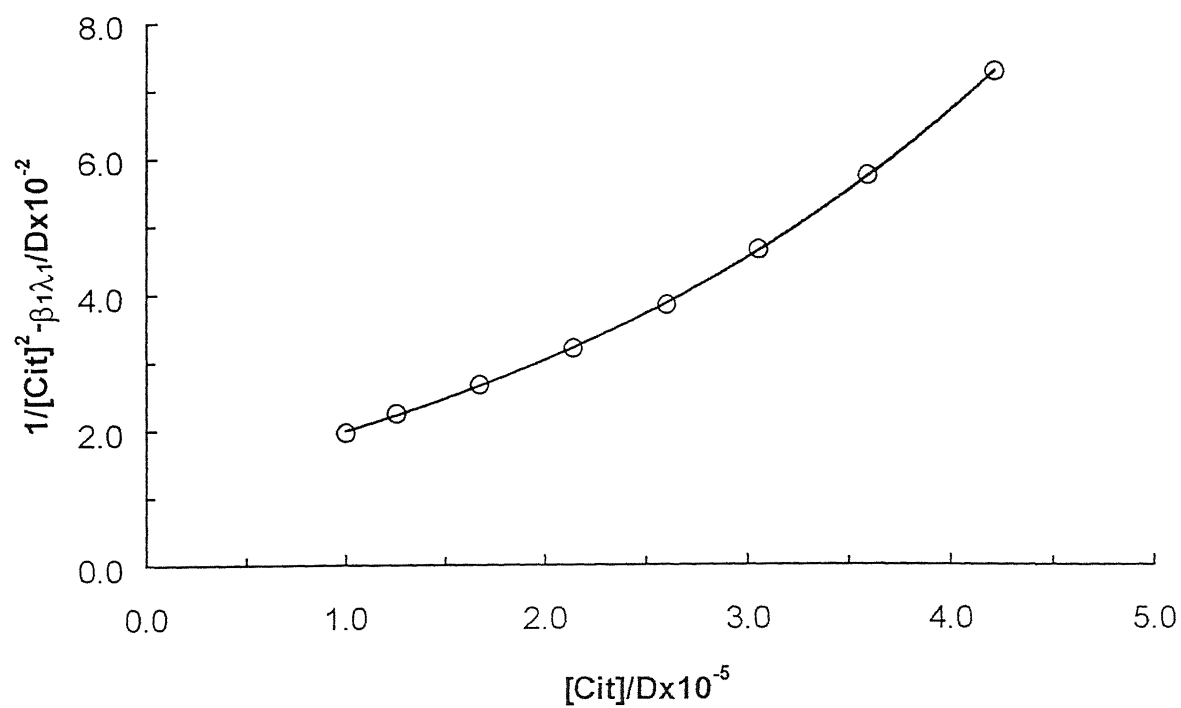
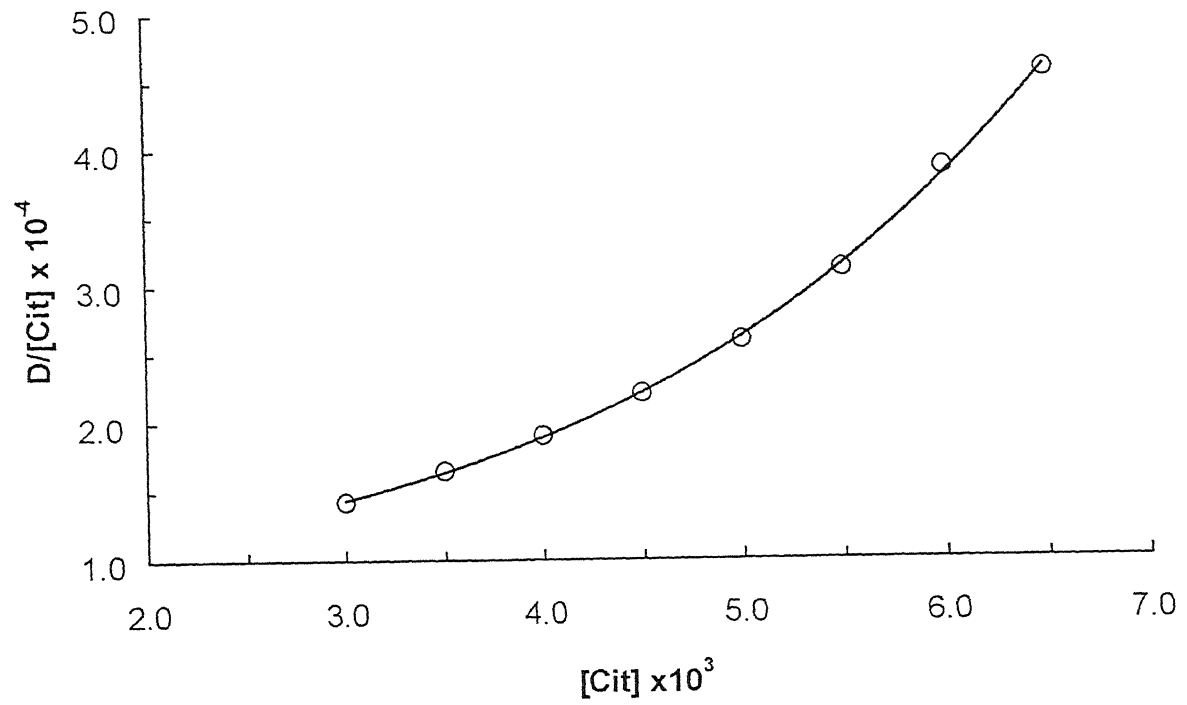


Fig. 4.22.a Plot of Co(II)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

D/[Cit] vs [Cit]



$1/[Cit] - \beta_{1\lambda_1}/D$ vs $[Cit]/D$

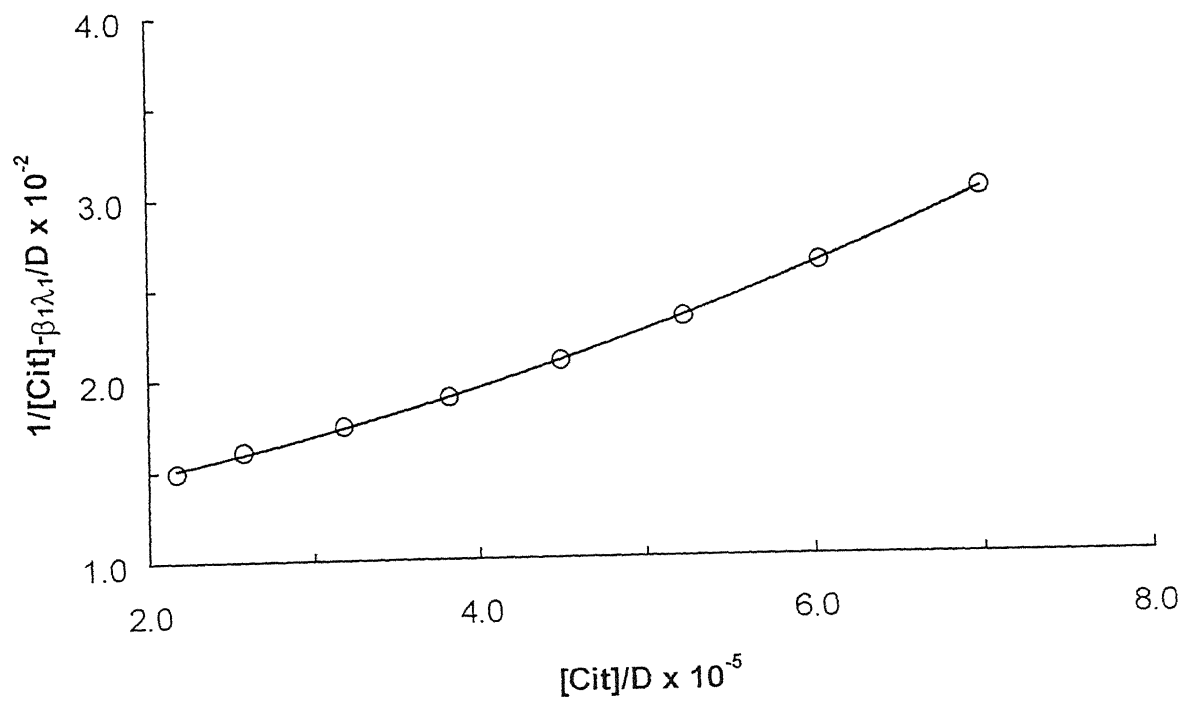
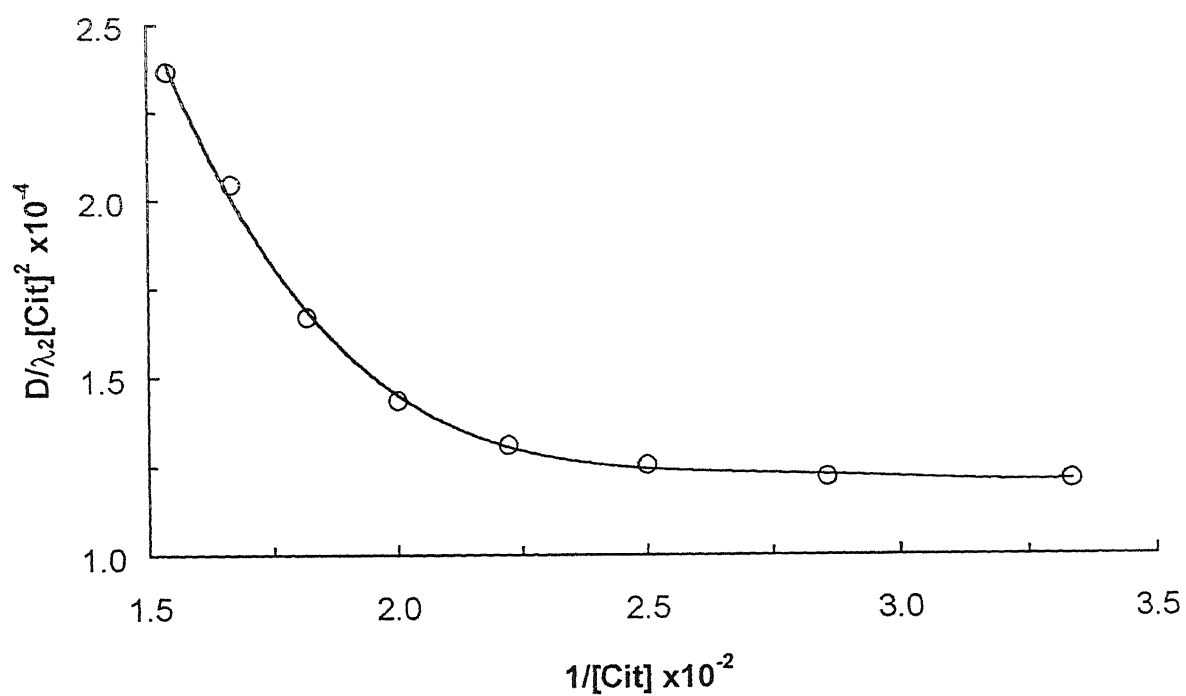


Fig. 4.21.b Plot of Ni(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

$D/\lambda_2[\text{Cit}]^2$ vs $1/[\text{Cit}]$



$D/[\text{Cit}]^2$ vs $1/[\text{Cit}]$

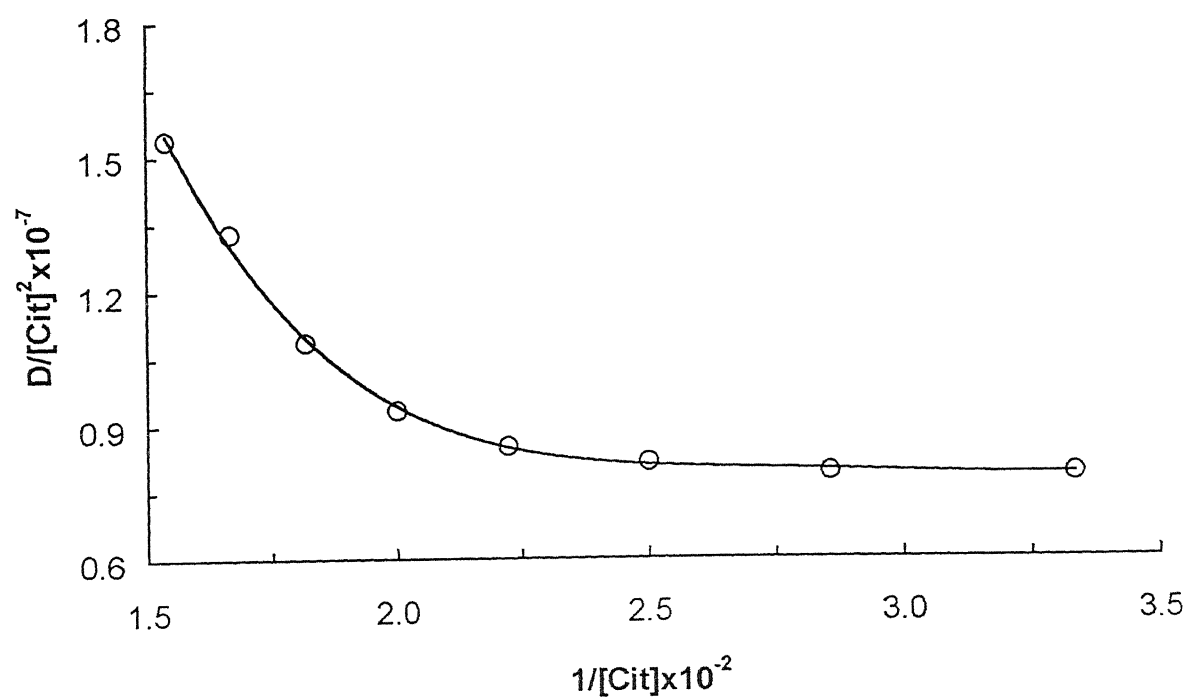
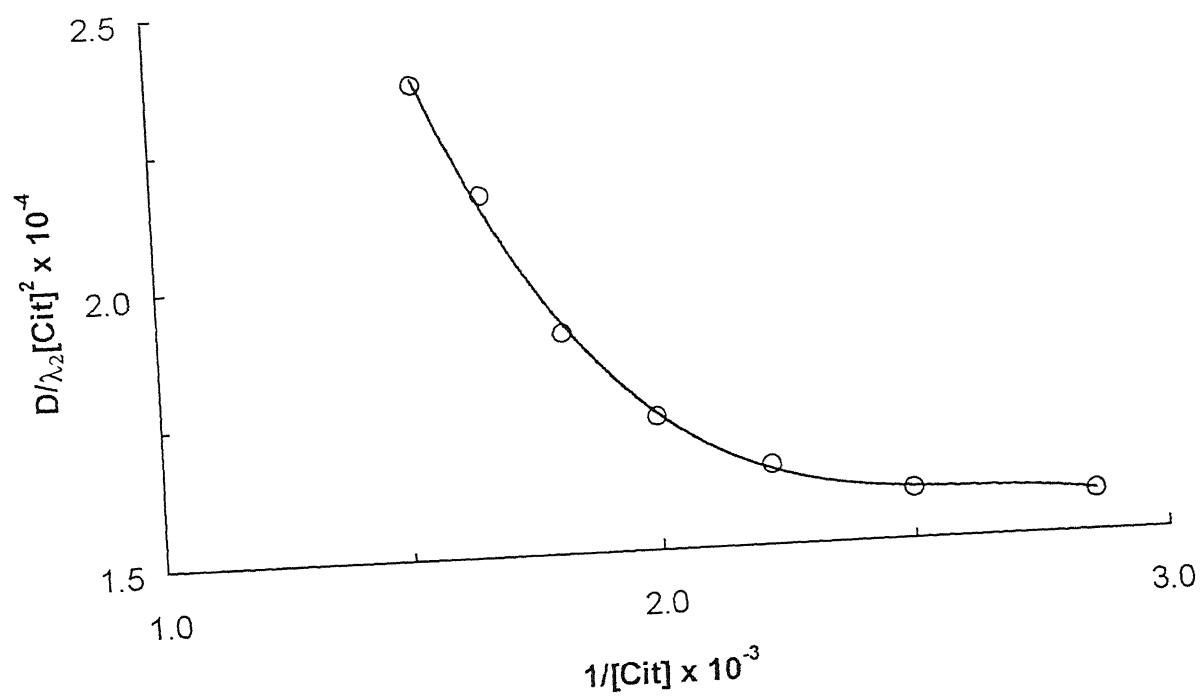


Fig. 4.22.b Plot of Co(II)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

$D/\lambda_2[\text{Cit}]^2$ vs $1/[\text{Cit}]$



$D/[\text{Cit}]^2$ vs $1/[\text{Cit}]$

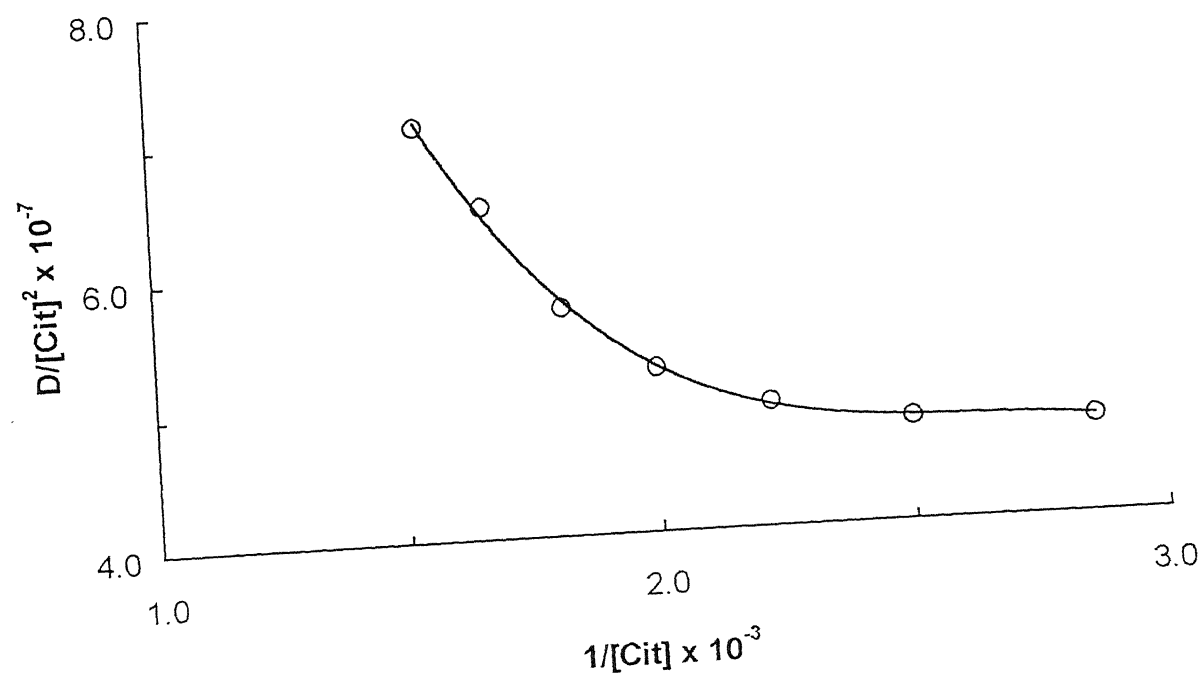
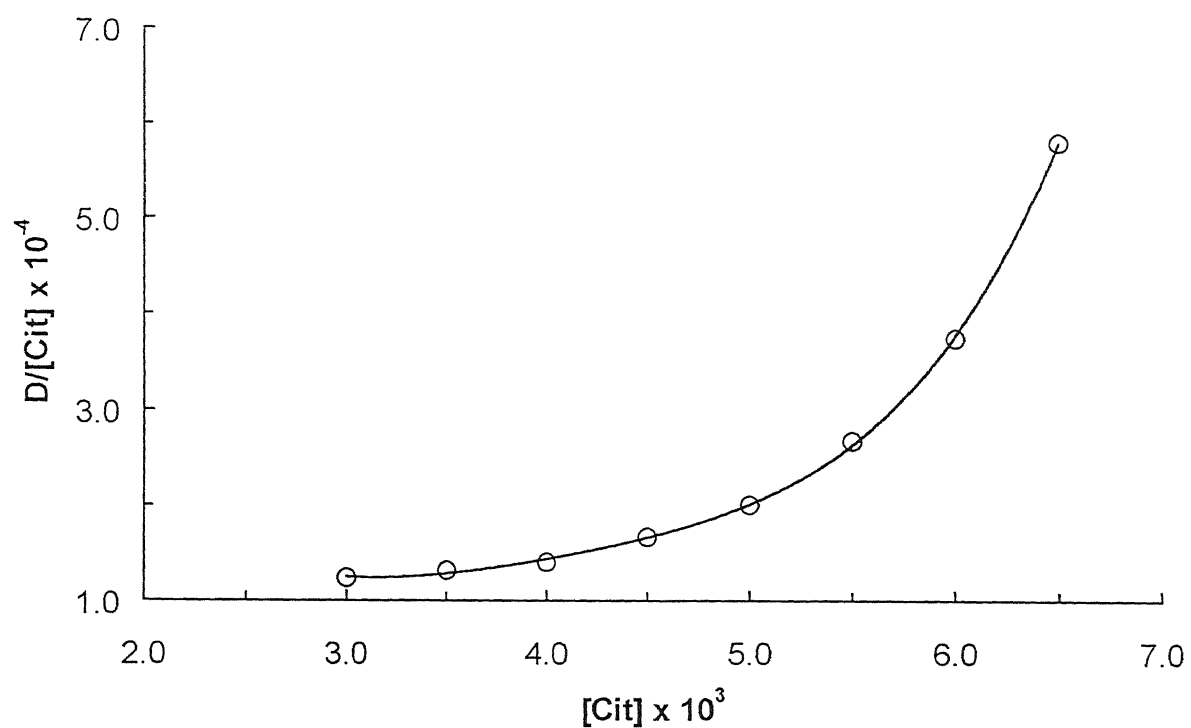


Fig. 4.23.a Plot of Cu(II)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

D/[Cit] vs [Cit]



$1/[Cit] - \beta_1 \lambda_1 / D$ vs $[Cit]/D$

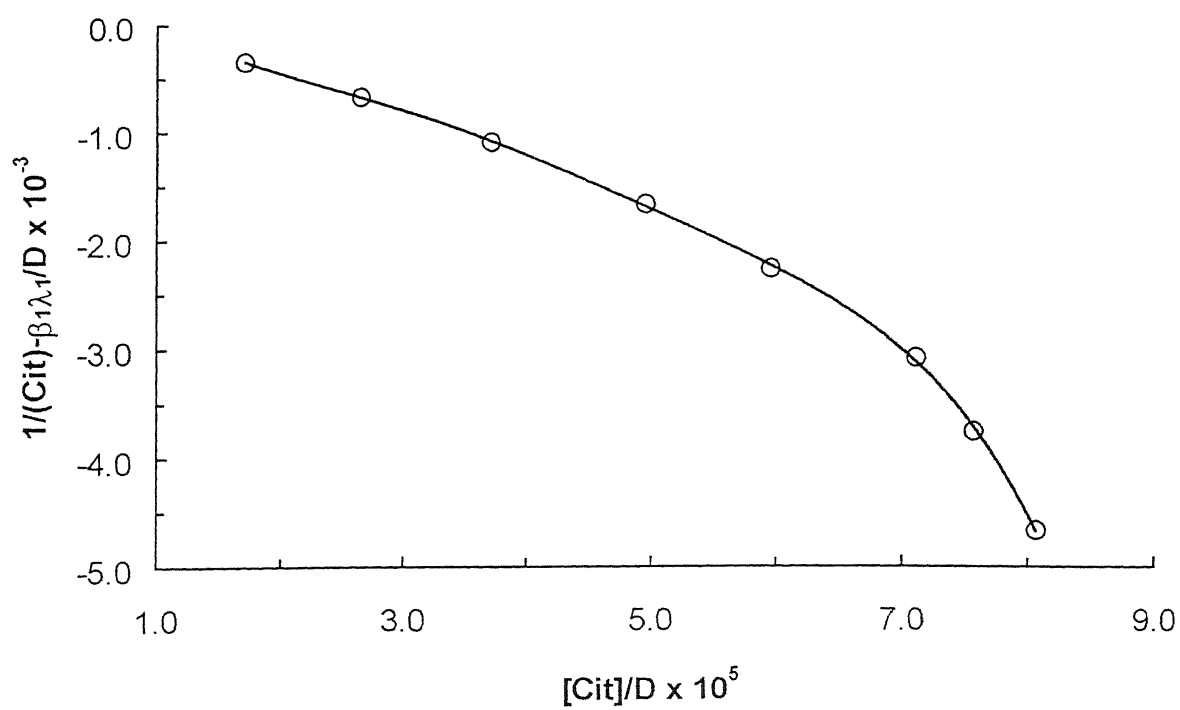


Fig. 4.23.b Plot of Cu(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

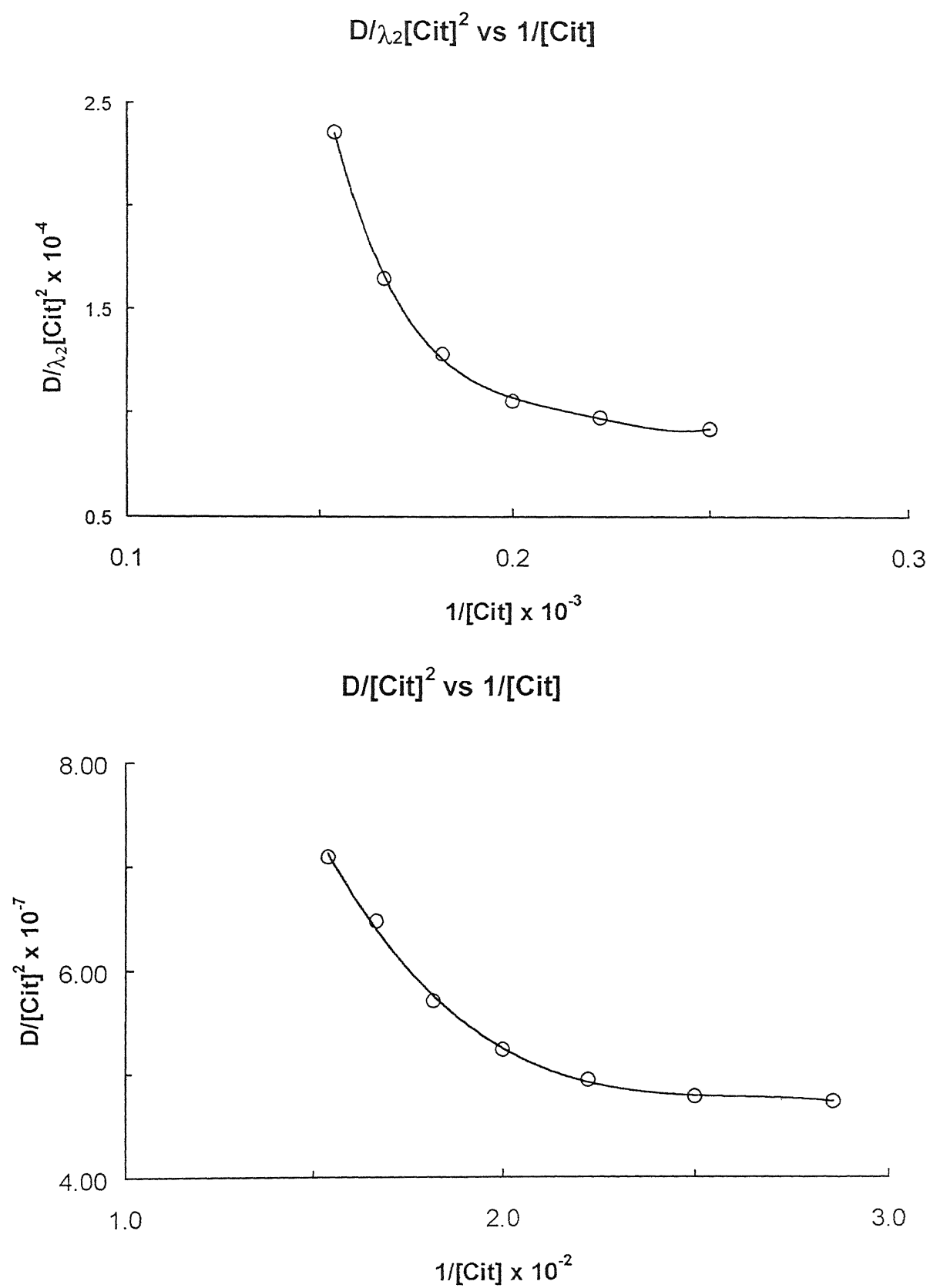
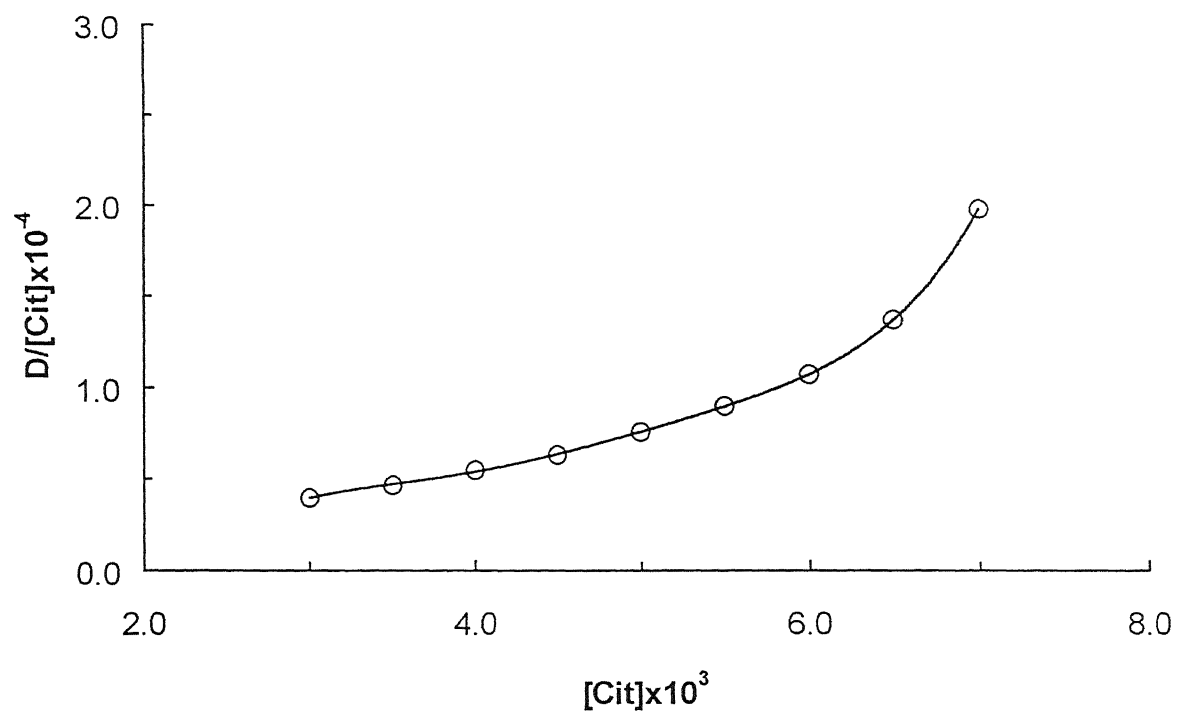


Fig. 4.24.a Plot of Zn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

$D/[\text{Cit}]$ vs $[\text{Cit}]$



$1/[\text{Cit}] - \beta_{1\lambda_1}/D$ vs $[\text{Cit}]/D$

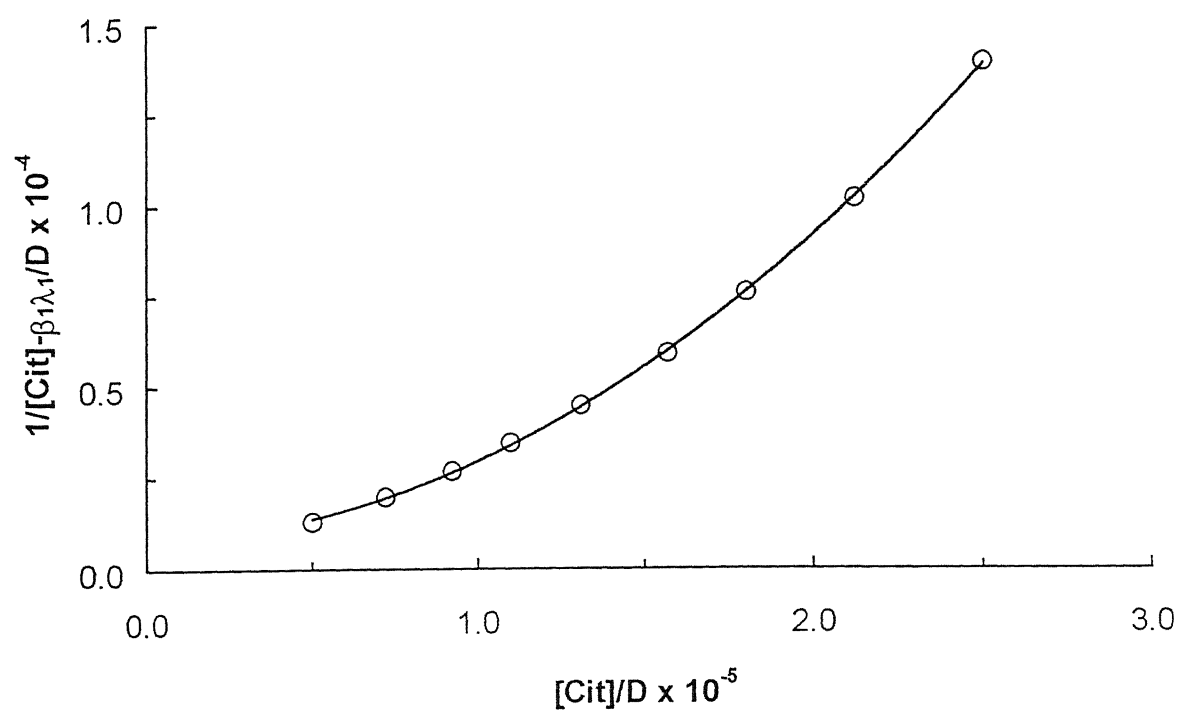


Fig. 4.24.b Plot of Zn(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

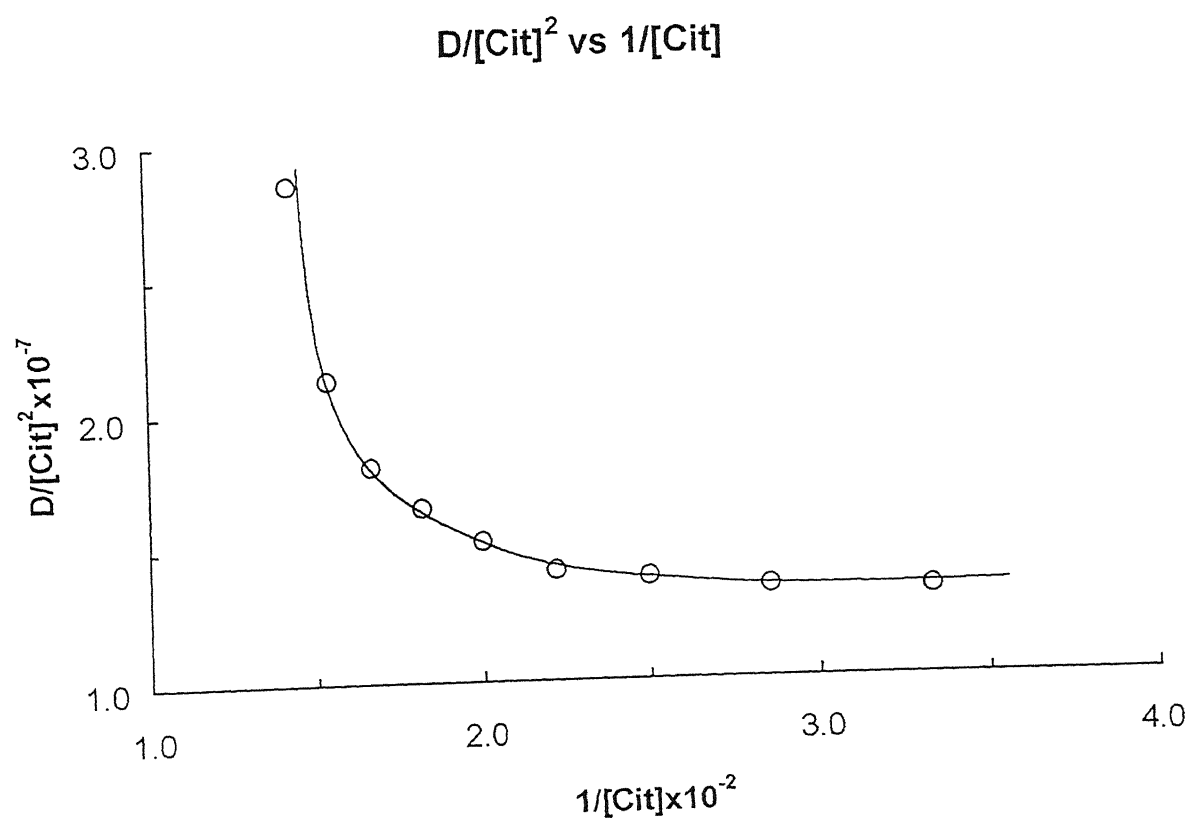
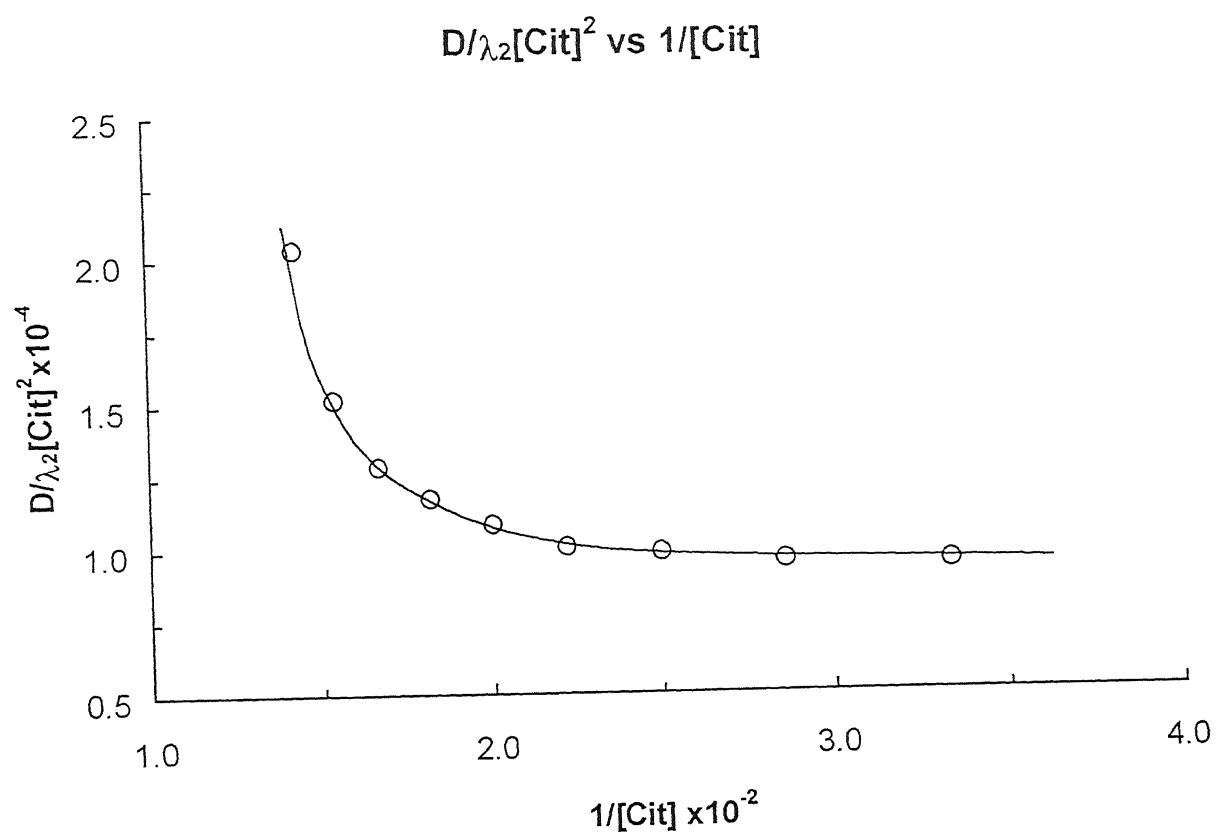
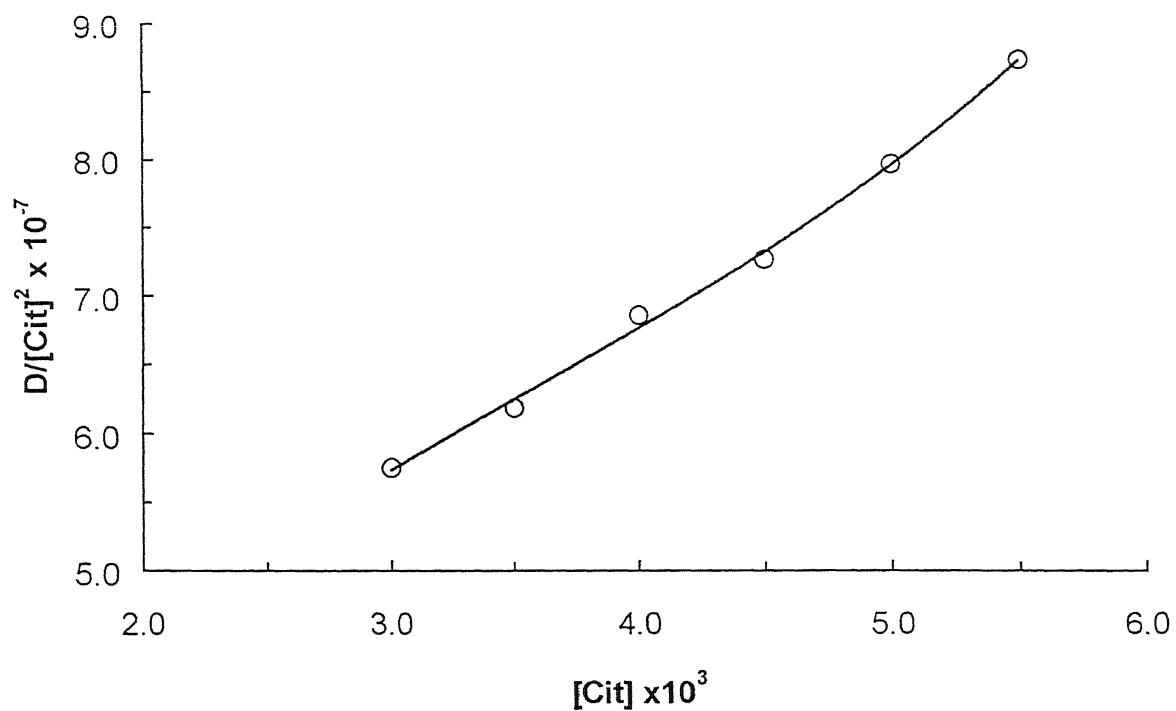


Fig. 4.25.a Plot of Cd(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

$D/[\text{Cit}]$ vs $[\text{Cit}]$



$1/[\text{Cit}] - \beta_{1\lambda_1}/D$ vs $[\text{Cit}]/D$

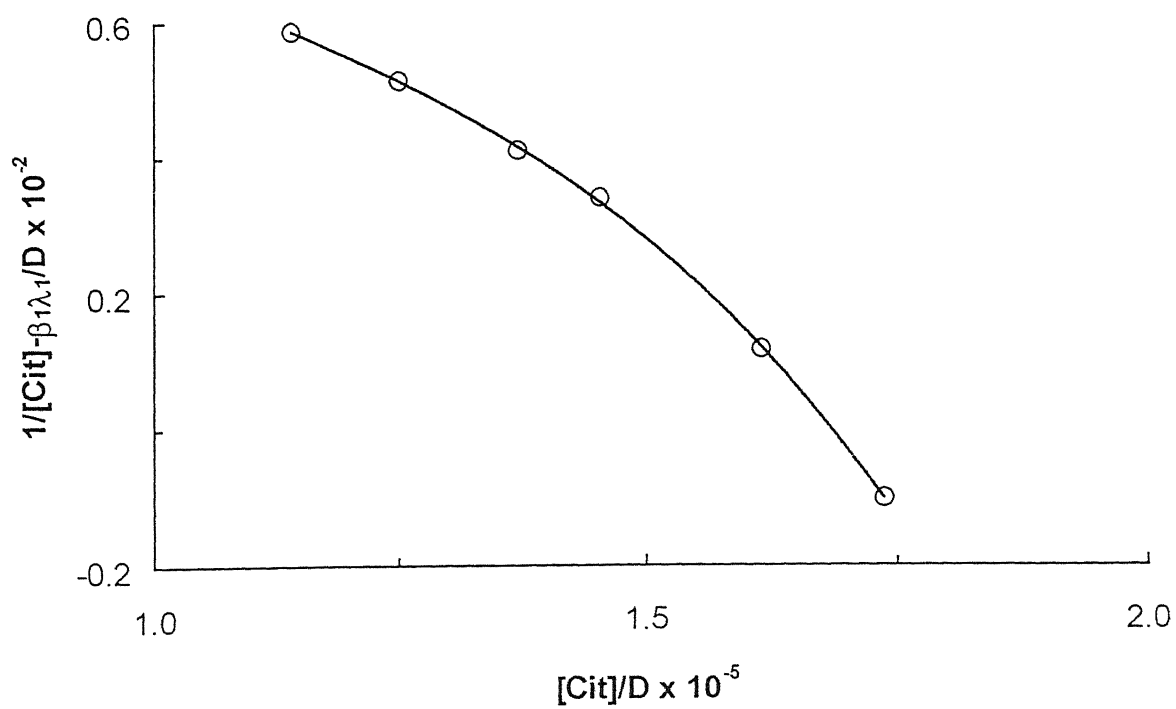
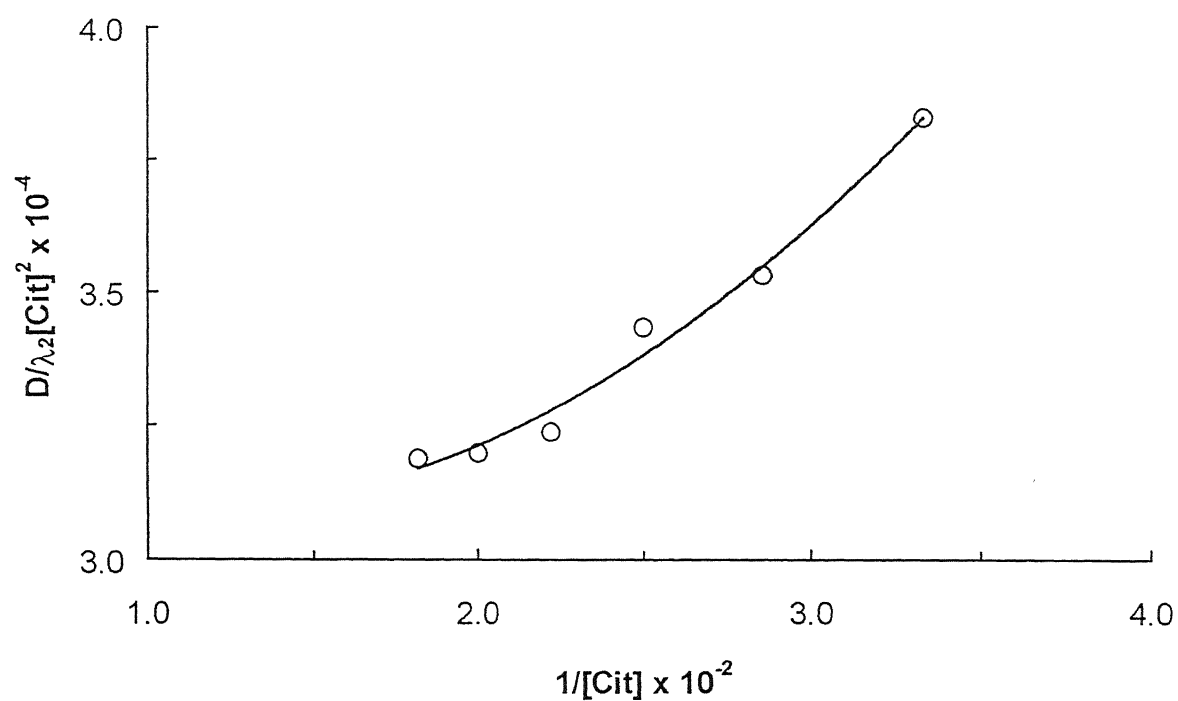


Fig. 4.25.b Plot of Cd(II)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

$D/\lambda_2[\text{Cit}]^2$ vs $1/[\text{Cit}]$



$D/[\text{Cit}]^2$ vs $1/[\text{Cit}]$

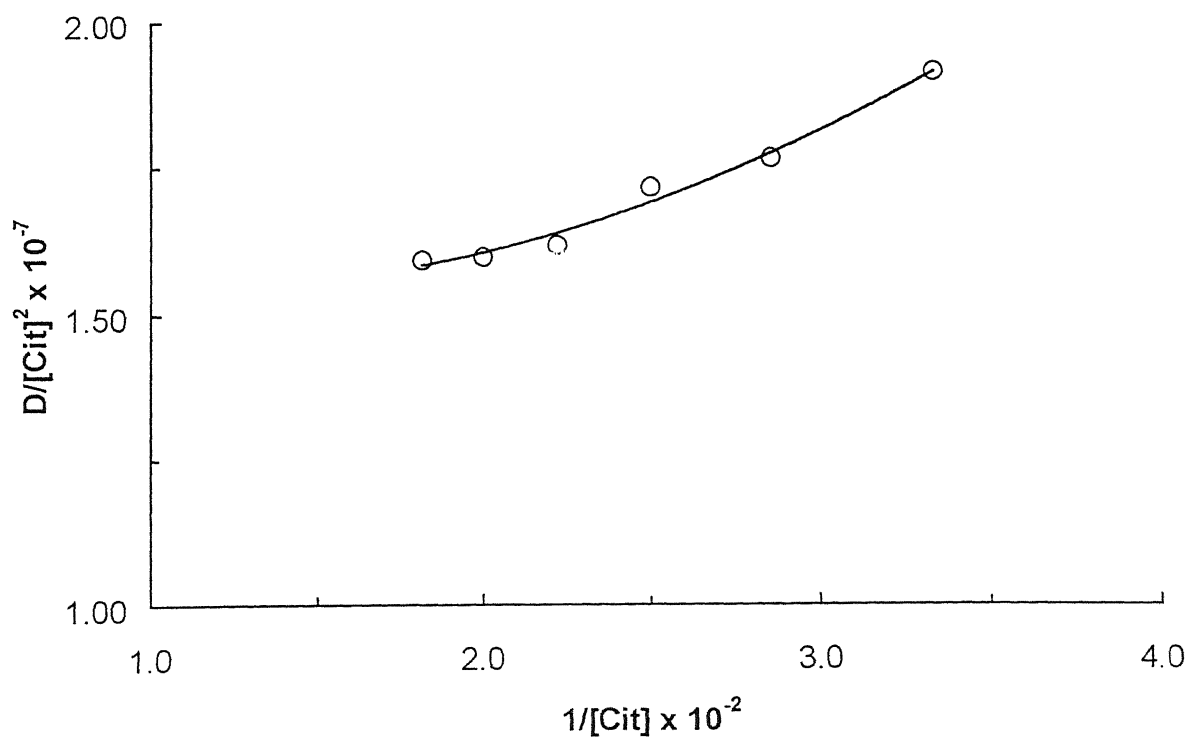


Fig. 4.26 Plot of $\text{Mg(II)}-(\text{NH}_4)_3\text{Cit(OH)}$ Amberlite IRA-400 system

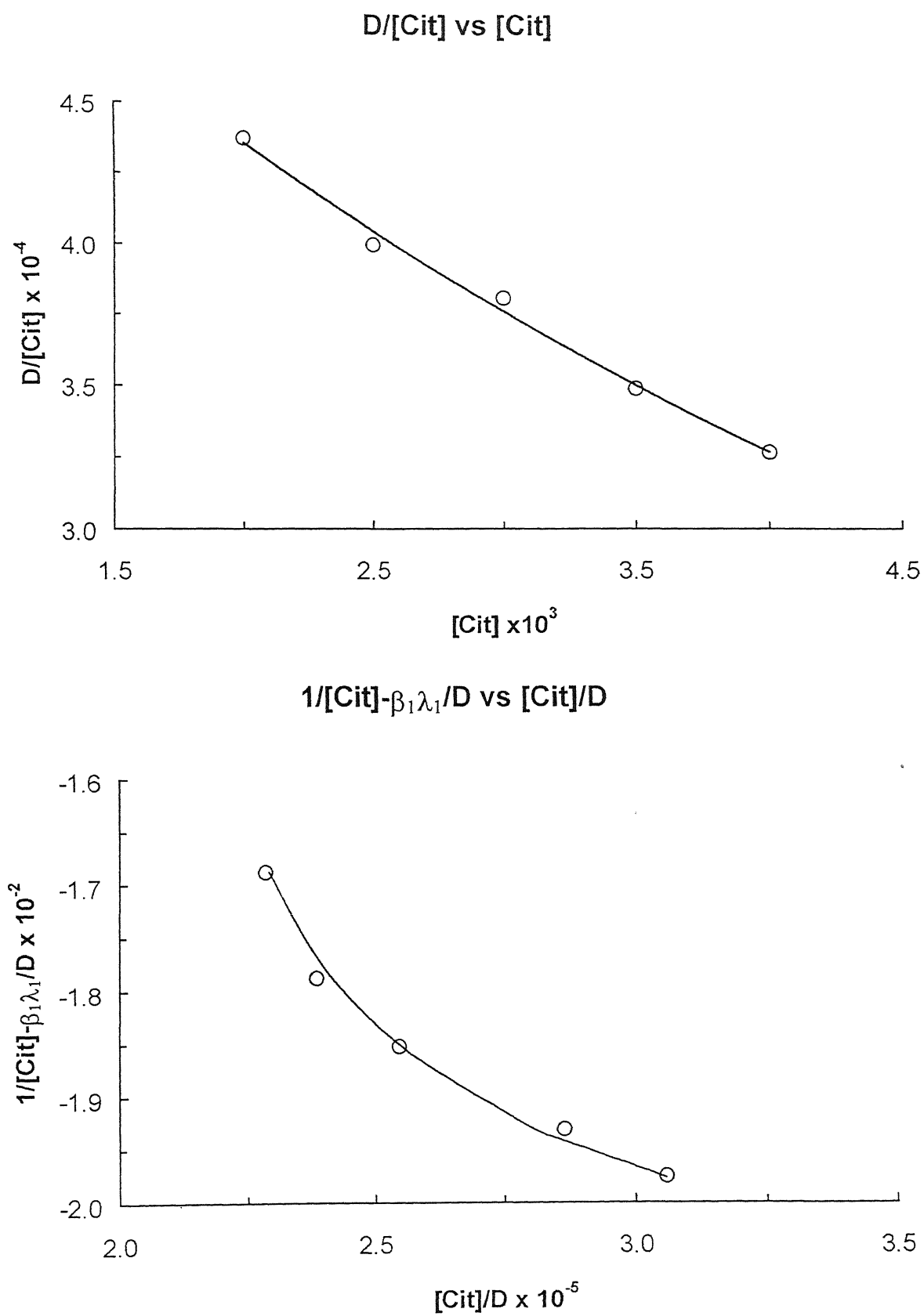


Fig. 4.27 Plot of Ca(II)-(NH₄)₃Cit(OH) Amberlite IRA-400 system

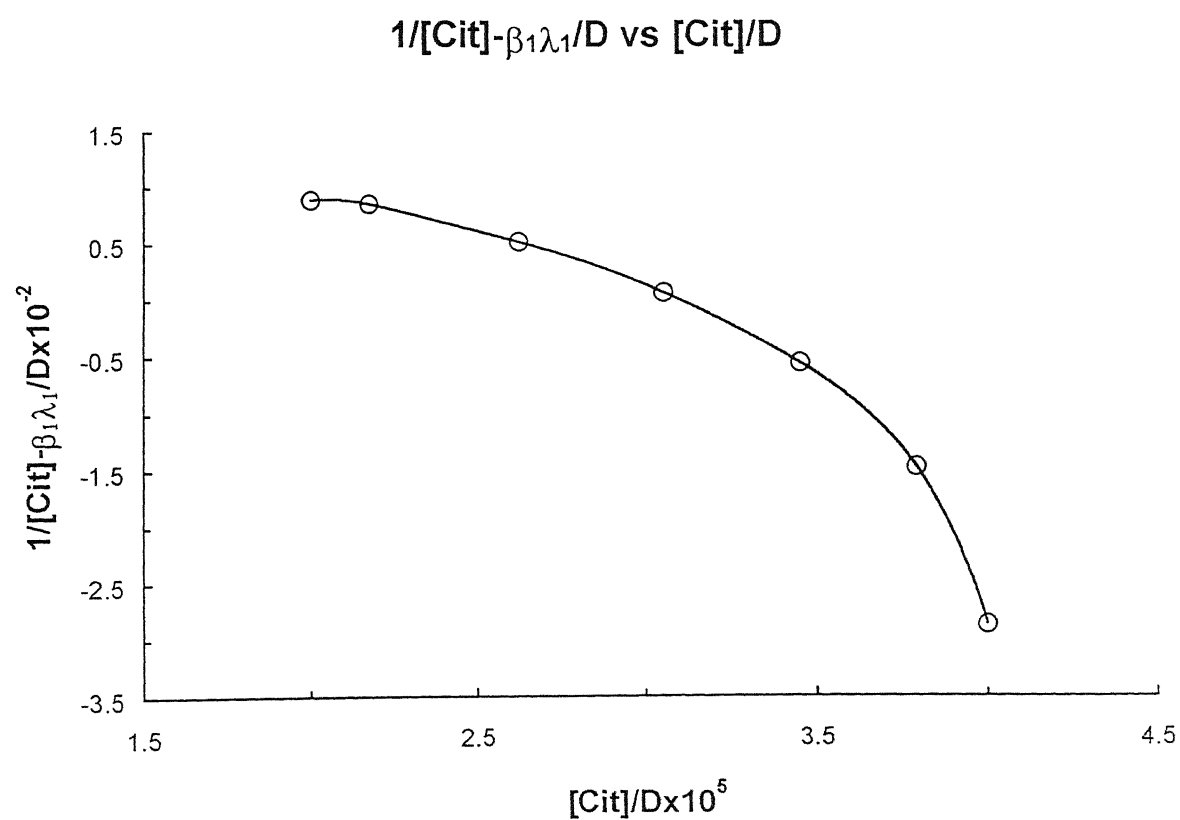
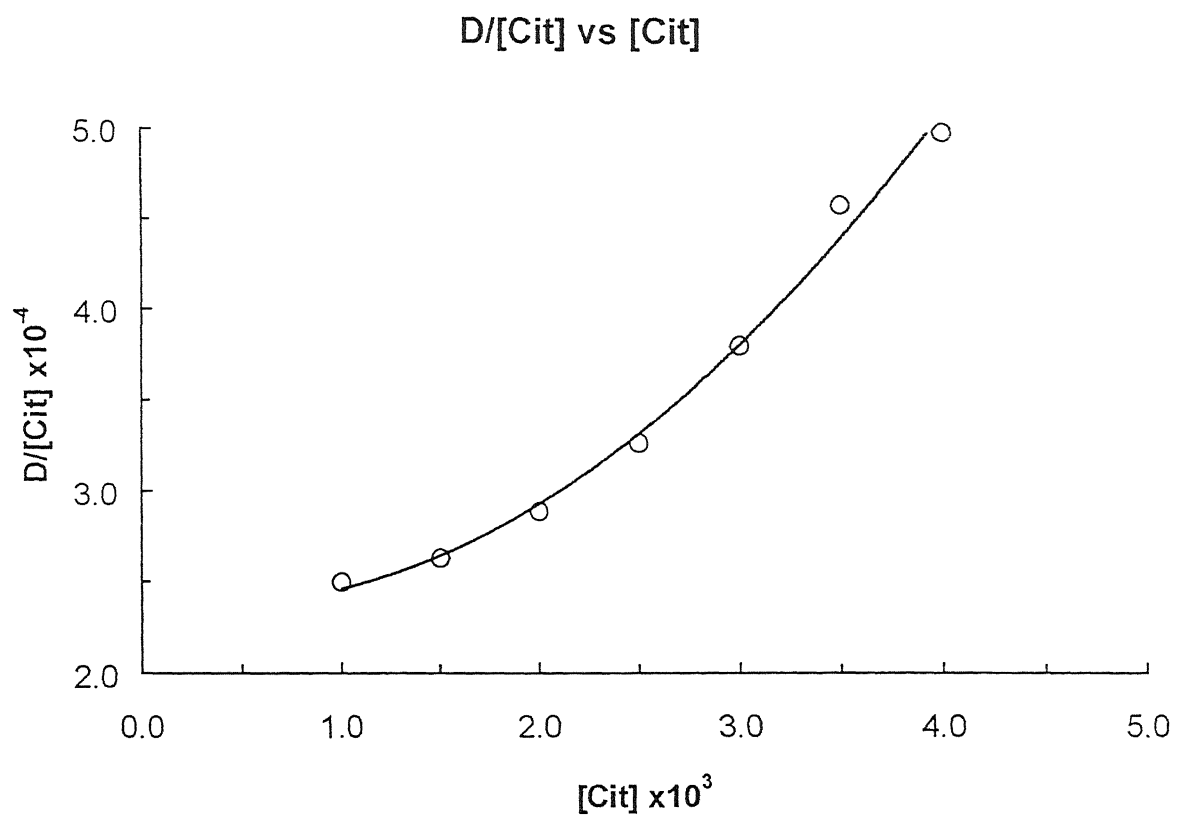
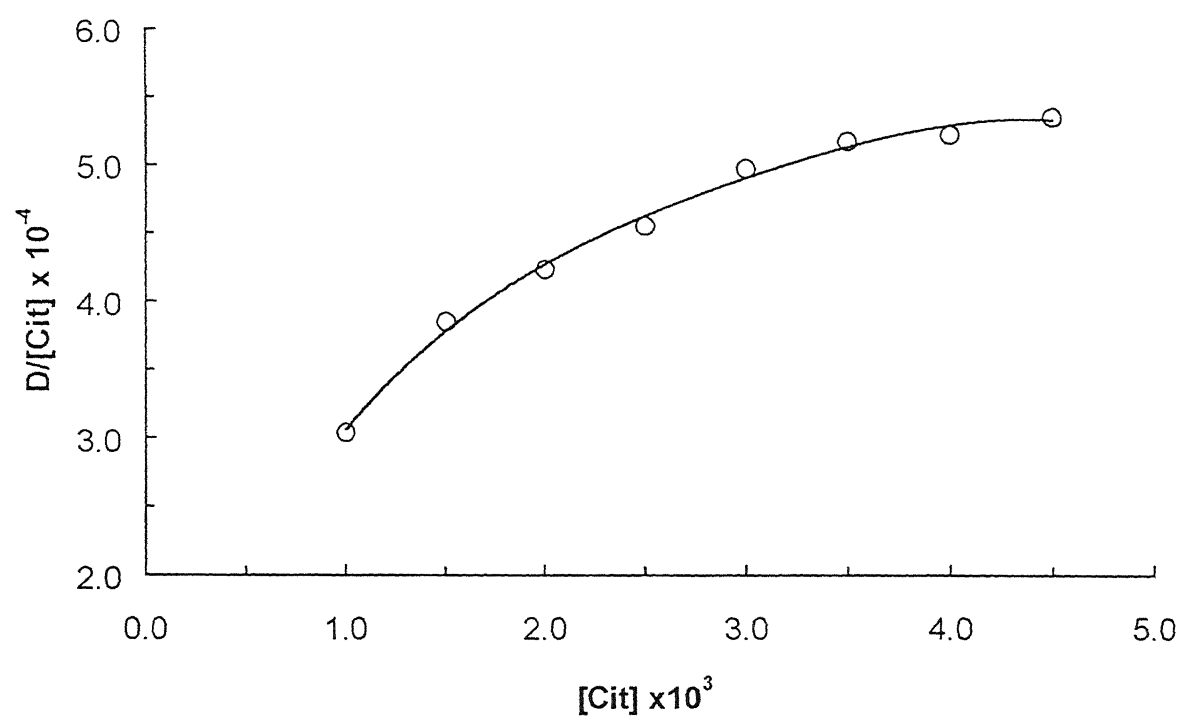
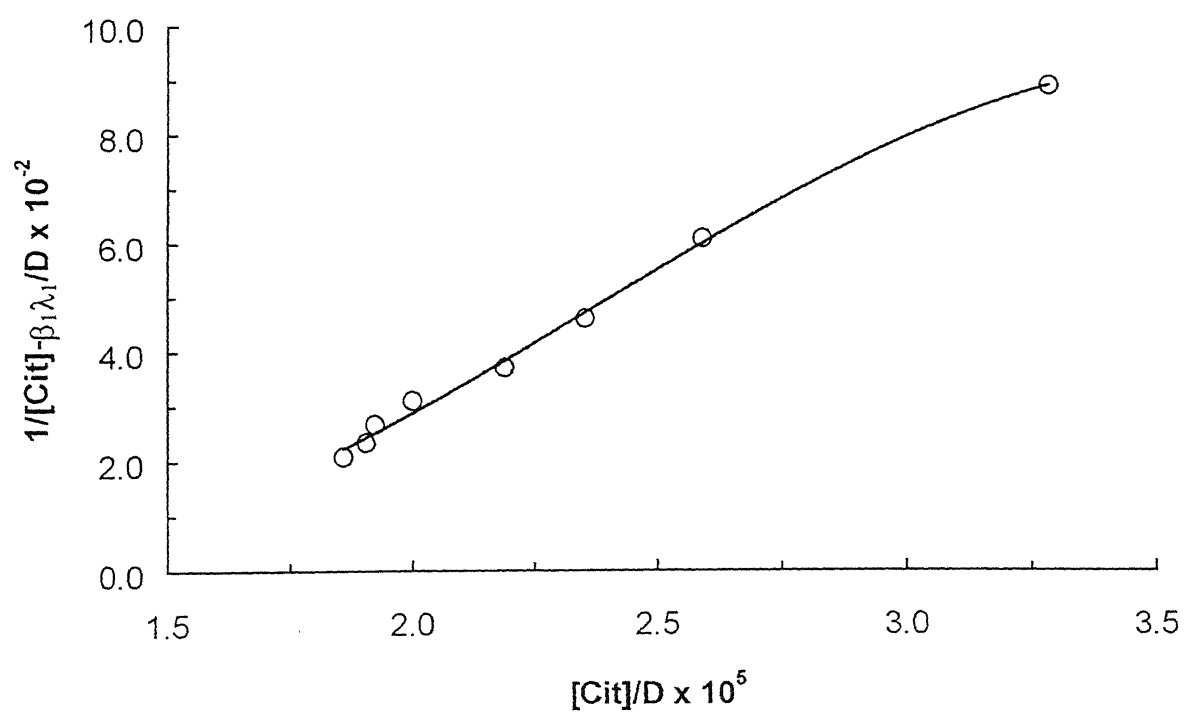


Fig. 4.28 Plot of Fe(II)- $(\text{NH}_4)_3\text{Cit}(\text{OH})$ Amberlite IRA-400 system

$D/[\text{Cit}]$ vs $[\text{Cit}]$



$1/[\text{Cit}] - \beta_1 \lambda_1 / D$ vs $[\text{Cit}] / D$



The sorption of metal ions onto the anion exchanger was occurring by the formation 1:1 and 1:2 anionic species. The values of individual distribution coefficients of the monovalent (λ_1) and bivalent (λ_2) anionic species evaluated which were used to calculate the formation constant of these systems Table 4.15, 4.17. The closeness of λ_1 values of Ni(II), Mg(II), Mn(II), Fe(II), Co(II), Ca(II), Zn(II), Cu(II), and Cd(II) metal ion species is due to $\text{MCit}(\text{OH})^{2-}$. But for Fe(III) the 1:1 species is not carrying negative charge or neutral, therefore, λ_1 value is insignificant. Similarly, the value of λ_2 in cases of bivalent ion species is due to $[\text{MCit}(\text{OH})]^{4-}$ and for Fe(III) is due to $[\text{Fe}\{\text{Cit}(\text{OH})\}_2]^{3-}$ species. The values of λ_1 and λ_2 are given in Table 4.15, 4.16.

Table 4.15:- Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal Ion	Experimental value λ_2	Calculated value λ_2	λ_1	β_2	β_1	Experiment-al value $\lambda_2\beta_2$	Calculated value $\lambda_2\beta_2$	$\lambda_1\beta_1$
Mg(II)	-	-	21.6	-	2709	-	-	58517
Ca(II)	-	-	2.26	-	10605	-	-	24015
Fe(II)	-	-	3.5	-	923	-	-	3243
Fe(III)	5900	5899	13354	196639	169	1160170100	1160167518	2261931
Mn(II)	328	328.5	17.6	21486	3339	7059655.02	7059679.9	59089
Ni(II)	650	650.0	-172	259316	165	168555400	168555415	-28344
Zn(II)	1400	1371.1	-5369	1195556	306	1673779408	1639333358	-1643312
Co(II)	300	257.4	10.7	124690	121	37407000	32093662	1304
Cu(II)	380	355.0	136.2	490308	1365	186317317	174069641	186042
Cd(II)	500	488.62	142.6	33618	415	16809000	16426508	59319

Table 4.15:- Log Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Met al Ion	Experime ntal value λ_2	Calculat- ed value λ_2	λ_1	β_2	β_1	Experiment al value $\lambda_2\beta_2$	Calculated value $\lambda_2\beta_2$	$\lambda_1\beta_1$
Mg(II)	-	-	1.33	-	3.43	-	-	4.77
Ca(II)	-	-	0.35	-	4.03	-	-	4.38
Fe(II)	-	-	0.54	-	2.97	-	-	3.51
Fe(III)	3.77	3.77	4.13	5.29	2.23	9.06	9.06	6.35
Mn(II)	2.52	2.52	1.25	4.33	3.52	6.85	6.85	4.77
Ni(II)	2.81	2.81	-	5.41	2.22	8.23	8.23	-
Zn(II)	3.15	3.14	-	6.08	2.49	9.22	9.21	-
Co(II)	2.48	2.41	1.03	5.10	2.08	7.57	7.51	3.12
Cu(II)	2.58	2.55	2.13	5.69	3.14	8.27	8.24	5.27
Cd(II)	2.70	2.69	2.15	4.53	2.62	7.23	7.22	4.77

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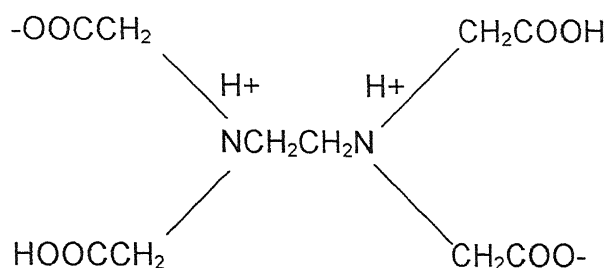
detd. simultaneously by potarogr. by using 0.5 citrate (pH 6.8) as supporting electrolyte.

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CHAPTER – 5

**ION EXCHANGE DISTRIBUTION EQUILIBRIUM
STUDY OF SOME BI-VALENT AND TRI-VALENT
METAL (ETHYLENEDIAMINETETRA ACETATE)
COMPLEX SPECIES IN SOLUTION**

Ethylenediaminetetraacetic acid is hexadentate ligand (12,29,77) and has many fold analytical application especially as a complexometric titrating agents (36,77). Its molecule a zwitter ion sometimes also described as double zwitter ion (19,77,36) because of the association of protons to both nitrogen atoms.



EDTA has six base sites and can combined with as many as six protons ($\text{H}_2 \text{EDTA}^{2+}$ in acidic medium) but the most loosely held protons appeared to be those on two of the acetate groups. There is strong practically supported evidence that the neutral EDTA molecule is a zwitter ion with two negative centers on the acetates and tow positive centers on the protonated nitrogen atoms. The protons associated with the nitrogen atoms are quite held and found to be last ones removed on the formation of tetranion, EDTA^{4-} complexes of metal ion always have 1:1 composition in normal experimental conditions (77,36,12,29) metal- EDTA complex are highly stable and the overall formation constants values are very high. The carbainion formation proceeds increasingly readily as the negative charge on the carboxylate, coo-group becomes less delocalised and more closely associated with the oxygen metal bond. The order of ease of carbanion formation for alkaline earth EDTA chelates in $\text{EDTA-Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ which is in accordance with transition metal ions this observed order is $\text{EDTA-Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$ and is radionalised in terms of the ligand field and the degree of covalent character of the oxygen metal bond (51). Bush and coworkers (59,10,78) have studied and an investigated the infrared spectra of et al EDTA (37) chalets and its derivative explaining the coordination aspects and the coordination number of involve metal ion species.

A variety of EDTA studies including the metal interactions have been investigated and described in the literature and the

monographs(12,29,36,10,51,19,59,77,78) The complexing titration of Th and rare earths with EDTA using semi methylthymol blue an methylthymol blue as a metallochromic indicators was reported at pH-2 and at pH 5.5-6 (hexamine-acetylacetone-acetone buffer solutions) respectively (10). But in another study of complexometry titration of Th(IV) and rare earth elements, pyrocatechol violet or semi xylenol orange indicators were used (1,12,19,29,51). EDTA reacts with Th(IV) ion in the molar ratio 1:1 Pd: EDTA at pH 3.7-8.9 was observed (21). The thallium was estimated by a replacement method of thallium (47) EDTA complex species by precipitation titration of thallium (47) chromate (48), indirect complexometric determination of thallium was reported using thiourea as masking agent(49), Xylenol orange was found successful indicator for Th (III) determination by EDTA (24) complexometric determination of Ga, In, Tl with EDTA using semimethyl blue thymol blue as the indicator has been reported by Mednal and workers(9). Sarkar and coworkers studied the effect of EDTA on the heavy metal complex of DNA. EDTA was found more effective in cases of silver and mercury posing compared to the chelating agents, phythin and deferoxamine(11). An equilibrium study of La(III)-EDTA-D(+) Saccharin acid system was reported by Panda et al. (60,30,42,74). Rao and coworkers used EDTA for the determination of chromium in trace amounts with other colour reagents (58). Planar chromatography of a number of metal-EDTA complexes on silica gel in layers have been investigated by Sharma and coworkers (52). The influence of ionic strength and hydroxide concentration on the Cu-EDTA complex species in alkaline medium has been studied by Norkers and coworkers(33). The kinetics and mechanism of oxidation of EDTA acids with alkaline hexacyanoferrate (III) was reported by Chaturvedi and coworkers (34). Ru(III)-EDTA catalyzed homogenous oxidation by molecular oxygen was reported by R.S.Shukla (63). Wand et. al determined chromium (VI) by ultrasonication using strong anion exchange solid phase extraction technique (53). A direct titration of Vanadium (IV) with EDTA-using N- Benzyle-N-Phynylhydroxylamine as metal indicator was reported (54). Dragon reported infrared spectroscopic determination of Pd-EDTA complex (62). Iron (III) is determined by its catalytic effects and inhibition separation of calcium an diphosphate through potentiometric mercury EDTA titration

(43). A biological investigation of EDTA in human cirime was reported by Qureshi and Bansal (57). Separation of Bi(III), Fe(III) an Cu(II) has been achieved by reversed phase chelate effects, then much stronger complexes could be formed by most metal cations. He found that the aminopoly carboxylic acids are excellent complexing agents. The most important of these in 1,-diaminoethantetra-acetic acid (ethylaminetetra acetic acid) and its sodium salts, the disodium salt is most avoidly employed in titrimetric analysis.

The simple 1:1 stoichiometry of metal-EDTA complex species with all metal ions, the availability of a number of metallochromic indicators, use of EDTA as a primary standard material and its strong complexation nature makes EDTA, to be used in various ways especially as complexmetric reagent for the determination of almost all complex forming metal ions, for most of the purposes the disodium salt of EDTA, $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ is found suitable instead of its acid. If high purity EDTA salt is not available or if an old standard solution needs to be restandardized, EDTA solutions then standardized with primary standard either CaCO_3 or Zn metal. For back titrations the excess of EDTA is evaluated using a standard solution by MgSO_4 or MgCl_2 (pH 10). But in acidic medium a standard solution of Zn or capper salt is used. Calcium and magnesium ions are found widely in many system including in animal cells and EDTA titrations are employed directly or with slight modification or prechemical treatments. It is used in the analysis of cirime, blood serum, egg shells, milk and many other such samples.

The Cu-EDTA complex interaction study form dealuminated scolecite was reported by Joshi and Banergee (28). An isotachophoretic separation of metal cations using EDTA as a chelating agent was reported by Hirokawa and coworkers(23). Nabi and coworkers studied the sorption of metal ion on modified anion-exchange resin and reported the selective separation of Hg(II) from other heavy metals(46). Symptomatic relief of angina pectoris was obtained when patients were treated for portaged periods with disodium deposited in atheroscle rotic plagnes in the corny arteries. Schwarzenbach(51,59,61) realized that the acetate ion is able to form acetato complexes of low stability with nearly all polyvalent cations, and that if this property could be reinforced by the but important application

of EDTA is that the biological fluids analyzed for sugar content then the sample is treated with an excess of alkaline copper (II) which is reduced to Cu_2O by the sugar, and the excess copper(II) is back titration with EDTA. This method of carrying out a reaction with excess metal ion and back-titration with EDTA can be applied to the analysis with mercury (II), e.g, nicotinaeide, phenobarbital and ethyl gallate several other compounds, such as caffeine, quinine, theine and thiamine, are precipitated as a salt of the anion BiI_4^- , and the excess bismuth (III) is titrated with EDTA, EDTA is used in the analysis of pigments for their cadmium, lead, and Zn contents. EDTA is widely used for the titration of many metal ions such as Al(III) , Bi(III) , Cd(II) , Zn(II) , Co(II) , Cu(II) , Mn(II) , Ni(II) , Sn(II) , Th(IV) , Tl(III) etc. other alkaline earth cations may also be estimated using suitable indicators by similar method. It is commonly used for evaluating the hardness water. This method of determining calcium and magnesium is also applied to the analysis of limestone, dolomite.

Usually in complexation studies by ion-exchange method relatively simple inorganic complexing ligands have been used. Gradually the systems with strong complexing ligands have also been investigated by application of ion-exchange resins, studies have been carried out in recent years to determine equilibrium data by exhaustive such studies of these complex ligand form resins and aqueous metal solution system (6,15,64,65,75). Some studies have also been carried out with other complexing resins (45) which have very high affinity for polyvalent cations, such resins contain carboxylate, sulphonate and methylenediphosphonate as the active groups of the resin prepared.

Considerable work on proton ligand and metal ligand equilibrium of EDTA in a number of binary complexing systems have been reported (2,3,8,16,25,27,26,33,34,35,41,66,68,72,73,76) Anatoly and coworkers determined the ion exchange behaviour of a sulfur-modified biotite towards Pb(II) , Hg(II) , Co(II) , Cu(II) , Cd(II) and Zn(II) and analyzed the concentration equilibrium constants as a function of metal loading (80). Muraviev and coworkers reported the ion-exchange equilibrium studies of Cu(II) and Zn(II) with iminodiacetic acid and aminomethyl phosphoric form resin(4). Determination of ion-exchange equilibrium constants of strongly acidic resins with alkaline earth metals using a potentiometer has been

reported by Norge and Arana(7). Awad and coworkers determined and evaluated the distribution coefficients of some mono, di- and tetravalent ion using Amberlite M-500 nitrate-form anion exchanger (250-420 mesh size)(5) Determination of equilibrium constant of Ca(II) , Cu(II) , Hg(II) and Pb(II) chelates with Dowex A-a chelating resin using ion selective electrode was reported by Harju and coworkers(24).

Present investigation describe a systematic study of Fe(II) , Fe(III) , Zn(II) , Cu(II) , Ni(II) , Co(II) , Ca(II) , Cd(II) , La(III) , Al(III) , Mg(II) which have been carried out with an Cl formed anion exchange reaction. The batch equilibrium technique was used for performing the equilibrium experiments. in this method the ion exchanger contact with a solution in a similar vessel while stirring or shaking. The ion exchanger reaction proceeds between the ion exchange and ions in solution is established. After equilibrium the exchanger is separated from the solution.

EXPERIMENTAL

- (1) **Metal Ion Solutions:-** stock solution (0.05m-0.1m) of Zn(II) , mg(II) , Fe(II) , Ni(II) , Co(II) , Ca(II) , Cd(II) , Fe(III) , La(III) , Cu(II) , were prepared individually from their reagent grade chloride or nitrate (or in some cases sulphates) samples. The compounds used were either of B.D.H., AnlaR, E.Merck, The prepared solution were then standardized by the method summarized in Table(3.1) Chapter 3
- (2) **Disodium salt of ethylenediaminetetra acetic acid(EDTA):-** As described in ch.3.
- (3) **Resins:-** Amberlite IR 400 anion exchanger were used as per details given is Ch.3

DISTRIBUTION STUDY

Present investigation describes a systematic study, which has been carried out with a Cl form anion exchange resin. The batch equilibration technique was used for performing the equilibrium experiments, and the ratio of the metal to ligand was kept. 1:1, The ligand disodium salt of EDTA was mixed with the metal solution, and resulting complex species solution was treated with 1000 anion exchanger (Amberlite IRA-400) resin in Cl-form, the overall volume of aqueous phase was kept

to 100mL. The flasks were shaken mechanically for 24 hours, and it was ascertained that this duration was adequate to attain the equilibrium. Thereafter the resin was filtered off and the chloride and hydrogen ion contents were determined in an aliquot of the filtrate by argentometry and acid base titration respectively. The distribution of metal-EDTA complex between the resin and the aqueous phase solution were worked out and the k_d - values were calculated.

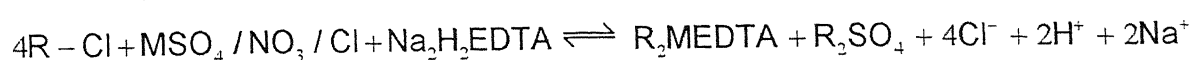
RESULT AND DISCUSSION

The sorption tendency of the anion metal-EDTA complex species for the metal ions Mg(II), Mn(II), Co(II), Ni(II), Cu(II), Pb(II), Al(III), have shown a gradual decrease with the increase of metal- EDTA concentrations. This behaviour may be co-related with the other exchanging species specially SO_4^{2-} or NO_3^- , which is showing stronger sorption, related to anions metal-complex species. But in cases of Fe(III) and Ca(II), instead of SO_4^{2-} or NO_3^- the chloride was co-anion, therefore, the possibility of the exchange of chloride is ruled out as resin or the anion exchanger was also taken in the Cl^- - form. The results for these Fe(III) and Ca(II) differ from the other above mentioned metal ions because anionic species of Fe (III) and of Ca(II) have shown a almost constant sorption throughout the investigated range. But the behaviour of La(III)- EDTA species is not following the trend either of both the metal ion groups described above, i.e, neither decreasing sorption pattern nor steady sorption, instead an increase in the sorption pattern has been observed, which may be contributed by its relatively much high affinity towards the anion exchanger in comparison to nitrate co-anion present in the solution. Also the nitrate is not indicating its high sorption related to chloride as has been observed in case of Pb(II), Al(III) which were taken as nitrate solution.

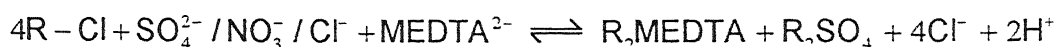
The complexation equilibria for the bivalent and the trivalent metal EDTA- Amberlite IRA-400 systems are given as.

I. Bivalent Metal – EDTA system:-

The complexation and the distribution of the species may be presented by the reactions,



and,



and by the application of law of mass action the ion exchange equilibrium constant (k) may be expressed as,

$$K = \frac{[R_2MEDTA][R_2SO_4][Cl^-]^4[H]^2}{[MEDTA^{2-}][SO_4^{2-}][R - Cl]^4} \text{ or,}$$

$$\lambda = \frac{[R_2MEDTA]}{[MEDTA^{2-}]}$$

$$K = \lambda \frac{[R_2SO_4][Cl^-]^4[H]^2}{[SO_4^{2-}][R - Cl]^4} \text{ or,}$$

Taking log

$$\log K - \log \lambda = \log[R_2SO_4] + 4\log[Cl^-] + 2\log[H^+] - 4\log[R - Cl]$$

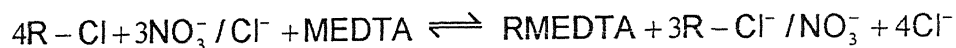
Sum of the quantities $\log K - \log \lambda = \log[R_2SO_4] + 4\log[Cl^-] + 2\log[H^+] - 4\log[R - Cl]$ is denoted as Z, then

$$\log K + Z = \log \lambda$$

The plot of Z Vs $\log \lambda$ at zero [L] concentration gives $\log K$ as limiting value of the intercept.

II. Trivalent Metal-EDTA system :-

The complexation and the distribution of the species may be presented by the reaction,



and by the application of law of mass action the ion exchange equilibrium constant (k) may be expressed as,

$$K = \frac{[RMEDTA][R - NO_3^-]^3[Cl^-]^4}{[MEDTA][NO_3^-]^3[R - Cl]^4} \text{ or,}$$

$$\lambda = \frac{[RMEDTA]}{[MEDTA^{2-}]}$$

(λ = Distribution coefficient of complex species, M-EDTA)

$$K = \lambda \frac{[R_2NO_3]^3 [Cl]^{-4}}{[NO_3^-]^3 [R - Cl]^4} \text{ or,}$$

Taking log

$$\log K - \log \lambda = 3 \log [R - NO_3] + 4 \log [Cl^-] - 4 \log [R - Cl]$$

$$\text{Sum of the quantities } \log K - \log \lambda = 3 \log [R - NO_3] + 4 \log [Cl^-] - 4 \log [R - Cl]$$

[is denoted as Z, then

$$\log K + Z = \log \lambda$$

The plot of Z Vs $\log \lambda$ at zero [L] concentration gives $\log K$ as limiting value of the intercept .

The distribution coefficient of the various metal-EDTA complex species, and the corresponding ion exchange equilibrium constant were evaluated with the help of equation and the related quantities used in various calculations are summarized in Tables 5.1,5.2,5.3,5.4,5.45,5.6,5.7,5.8,5.9,5.10. The desired plots of various metal ions for calculating the ion exchange equilibrium constants are presented as Fig. 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 5.10

An ion exchanger may be considered possessing a very strong electrovalent or ionic character but its lattice is not comparable with an ionic compound, because the cationic and anionic parts are not of the same magnitude. The exchange sorption may be to some extent described as like polyvalent cation or anion of cation and anion exchanger respectively, but the positive or negative charge is very high due to large number of exchangeable sites. Therefore the cation or the anion of an ion exchanger is definitely possessing a unique character and associated counter ions, and not by breaking of ionic form in case of electrovalent perform, which may also occur by polarizing effect of solvolysis.

Table-5.1: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Ca-EDTA complex

[ML] initially taken (x) $\times 10^4\text{M}$	[H ⁺] initially present in metal solution (a) $\times 10^4\text{M}$	[H ⁺] found after equilibrium (b) $\times 10^4\text{M}$	[H ⁺] remain (c) $= b - a$ $\times 10^4\text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4\text{M}$	[Cl ⁻] present in metal solution q_1 $\times 10^4\text{M}$	[Cl ⁻] present in acid solution q_2 $\times 10^4\text{M}$	[Cl ⁻] present before equilibrium $q = q_1 + q_2$ $\times 10^4\text{M}$	[Cl ⁻] remain $r = p - q$ $\times 10^4\text{M}$	[R ₂ CaEDTA] $= 1/2$ of remain [Cl ⁻] y $\times 10^4\text{M}$	[CaEDTA] _{aq} $= x - y$ $\times 10^4\text{M}$	λ	Log λ
20.0	2.4	8.0	5.6	75.0	40.0	2.4	42.4	32.6	16.3	3.7	440.5	2.64
25.0	3.0	8.6	5.6	93.8	50.0	3.0	53.0	40.6	20.3	4.7	433.4	2.64
30.0	3.6	9.2	5.6	112.5	60.0	3.6	63.6	48.6	24.3	5.7	426.3	2.63
35.0	4.2	9.7	7.2	131.3	70.0	4.2	74.2	56.9	28.5	6.6	433.4	2.64
40.0	4.8	10.1	8.7	150.0	80.0	4.8	84.8	65.2	32.6	7.4	440.5	2.64
45.0	5.4	10.8	7.1	161.6	90.0	5.4	95.4	66.2	39.5	11.9	322.7	2.64
50.0	6.0	11.4	5.4	173.2	100.0	6.0	106.0	67.2	46.4	16.4	204.8	2.63
55.0	6.6	12.0	5.4	196.6	110.0	6.6	116.6	80.0	48.6	15.0	309.8	2.62
60.0	7.2	12.5	5.3	220.0	120.0	7.2	127.2	92.8	50.8	13.6	414.7	2.62

Log value of variables {[R-Cl]}_{capacity of resin} = 264.5}

[Cl ⁻] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - r $\times 10^2$	logCl	logH	Log(R-Cl) _r	Z
32.6	5.6	232.4	-2.49	-3.25	-1.63	-9.92
40.6	5.6	224.4	-2.39	-3.25	-1.65	-9.47
48.6	5.6	216.4	-2.31	-3.25	-1.66	-9.10
56.9	7.1	208.1	-2.24	-3.15	-1.68	-8.54
65.2	8.7	199.8	-2.19	-3.06	-1.70	-8.07
66.2	7.0	198.8	-2.18	-3.15	-1.70	-8.21
67.2	5.4	197.8	-2.17	-3.27	-1.70	-8.41
80.0	5.3	185.0	-2.10	-3.53	-1.73	-8.51
92.8	5.3	172.2	-2.03	-4.28	-1.76	-9.63

Table-5.2: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Fe(III)- EDTA complex

[ML] initially taken (x) $\times 10^4\text{M}$	[H+] initially present in metal solution (a) $\times 10^4\text{M}$	[H+] found after equilibrium (b) $\times 10^4\text{M}$	[H ⁺] remain (c) $= b - a$ $\times 10^4\text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4\text{M}$	[Cl ⁻] present in metal solution q_1 $\times 10^4\text{M}$	[Cl ⁻] present in acid solution q_2 $\times 10^4\text{M}$	[Cl ⁻] present before equilibrium $q = q_1 + q_2$ $\times 10^4\text{M}$	[Cl ⁻] remain $r = p - q$ $\times 10^4\text{M}$	[R ₂ FeEDTA]= remain [Cl ⁻] y $\times 10^4\text{M}$	[FeEDTA] _{aq} $= x - y$ $\times 10^4\text{M}$	λ	Log λ
20.0	9.8	44.0	34.1	100.0	60.0	9.8	69.8	30.1	30.1	-	-	-
25.0	12.3	62.6	50.2	112.5	75.0	12.3	87.3	25.2	25.2	4.8	105.8	2.02
30.0	14.7	81.1	66.3	125.0	90.0	14.7	104.7	20.3	20.3	9.6	211.5	2.33
35.0	17.2	99.6	82.4	142.5	105.0	17.2	122.2	20.5	20.5	14.5	158.8	2.20
40.0	19.6	118.0	98.5	160.0	120.0	19.6	139.6	20.6	20.6	19.4	106.1	2.03
45.0	22.1	134.5	112.3	180.0	135.0	22.1	157.1	23.5	23.5	21.5	109.0	2.04
50.0	24.5	151.0	126.0	200.0	150.0	24.5	174.5	26.4	26.4	23.6	111.8	2.05
55.0	27.0	167.5	140.0	220.0	165.0	27.0	192.0	28.9	28.9	26.1	110.8	2.04
60.0	29.4	184.0	154.0	240.0	180.0	29.4	209.4	31.4	31.4	28.6	109.7	2.04

Log value of variables {[R-Cl]}_{capacity of resin} = 264.5}

[Cl] $\times 10^4$	(R-Cl) _r = (R-Cl) - r $\times 10^2$	logCl	Log(R-Cl) _r	Z
30.2	234.8	-2.52	-1.63	-3.56
25.3	239.7	-2.60	-1.62	-3.91
20.4	244.6	-2.69	-1.61	-4.32
20.5	244.5	-2.69	-1.61	-4.31
20.6	244.4	-2.69	-1.61	-4.30
23.5	241.5	-2.63	-1.62	-4.05
26.4	238.6	-2.58	-1.62	-3.82
28.9	236.1	-2.54	-1.63	-3.65
31.4	233.6	-2.50	-1.63	-3.49

Table-5.3: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Mn-EDTA complex

[ML] initially taken (x) $\times 10^4\text{M}$	[H ⁺] initially present in metal solution (a) $\times 10^4\text{M}$	[H ⁺] found after equilibrium (b) $\times 10^4\text{M}$	[H ⁺] remain (c) $= b - a$ $\times 10^4\text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4\text{M}$	[SO ₄ ²⁻] present in metal solution $q_1 \times 10^4\text{M}$	[SO ₄ ²⁻] present in acid solution q_2 $\times 10^4\text{M}$	[SO ₄ ²⁻] present before equilibrium $q = q_1 + q_2$ $\times 10^4\text{M}$	[Cl ⁻] liberated against SO ₄ ²⁻ (Q)= $2 \times q$ $\times 10^4\text{M}$	[Cl ⁻] remain $r = p - Q$ $\times 10^4\text{M}$	[R ₂ MnEDTA] =1/2 of remain [Cl ⁻] y $\times 10^4\text{M}$	[MnEDTA] _{aq} =x-y $\times 10^4\text{M}$	λ	Log λ
20.0	0.56	10.4	9.8	72.8	20.0	0.28	20.3	40.5	31.4	15.5	4.28	367.3	2.57
25.0	0.70	14.1	13.4	93.9	25.0	0.35	25.4	51.2	42.8	21.3	3.63	638.7	2.81
30.0	0.84	17.7	16.9	114.9	30.0	0.42	30.4	61.8	54.2	27.0	2.97	910.1	2.96
35.0	0.98	21.2	20.2	132.6	35.0	0.49	35.5	71.5	61.6	30.8	4.22	833.8	2.92
40.0	1.12	24.7	23.4	150.2	40.0	0.56	40.5	81.1	69.0	34.5	5.46	757.4	2.88
45.0	1.26	27.8	26.0	162.7	45.0	0.63	45.6	91.3	71.0	35.7	9.28	519.5	2.72
50.0	1.40	30.8	28.6	175.2	50.0	0.70	50.7	101.4	73.0	36.9	13.10	281.6	2.45
55.0	1.54	34.0	32.1	188.2	55.0	1.02	55.5	111.1	76.7	38.6	16.45	242.4	2.38
60.0	1.68	37.2	35.5	201.1	60.0	1.34	60.3	120.7	80.4	40.2	19.80	203.1	2.31

Log value of variables {[R-Cl]}_{capacity of resin} =264.5}

[Cl] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - rx10 ²	logCl	logH	Log(R-Cl) _r	Z
32.6	5.6	232.4	-2.49	-3.25	-1.63	-9.92
40.6	5.6	224.4	-2.39	-3.25	-1.65	-9.47
48.6	5.6	216.4	-2.31	-3.25	-1.66	-9.10
56.9	7.1	208.1	-2.24	-3.15	-1.68	-8.54
65.2	8.7	199.8	-2.19	-3.06	-1.70	-8.07
66.2	7.0	198.8	-2.18	-3.15	-1.70	-8.21
67.2	5.4	197.8	-2.17	-3.27	-1.70	-8.41
80.0	5.3	185.0	-2.10	-3.53	-1.73	-8.51
92.8	5.3	172.2	-2.03	-4.28	-1.76	-9.63

Table-5.4: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Mg-EDTA complex

[ML] initially taken (x) $\times 10^4 \text{M}$	[H ⁺] initially present in metal solution (a) $\times 10^4 \text{M}$	[H ⁺] found after equilibrium (b) $\times 10^4 \text{M}$	[H ⁺] remain (c) $=b-a$ $\times 10^4 \text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in metal solution q ₁ $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in acid solution q ₂ $\times 10^4 \text{M}$	[SO ₄ ²⁻] present before equilibrium m q=q ₁ +q ₂ $\times 10^4 \text{M}$	[Cl ⁻] liberated against SO ₄ ²⁻ (Q)= 2 x q $\times 10^4 \text{M}$	[Cl ⁻] remain r =p-Q $\times 10^4 \text{M}$	[R ₂ MgEDTA] =1/2of remain [Cl ⁻] y $\times 10^4 \text{M}$	[MgEDTA] _{aq} =x-y $\times 10^4 \text{M}$	λ	Log λ
20.0	1.2	28.0	26.8	80.5	20.0	0.6	20.6	41.2	39.4	19.7	0.3	2122.0	3.33
25.0	1.5	50.0	48.5	99.3	25.0	0.8	25.8	51.5	47.9	23.9	1.1	1826.0	3.26
30.0	1.8	72.0	70.2	118.1	30.0	0.9	30.9	61.8	56.3	28.1	1.8	1530.0	3.18
35.0	2.1	94.0	91.9	137.0	35.0	1.1	36.1	72.1	64.9	32.4	2.6	1321.0	3.12
40.0	2.4	116.0	113.6	155.9	40.5	1.2	41.2	82.4	73.4	36.7	3.3	1112.0	3.05
45.0	2.7	139.5	136.7	174.2	45.0	1.4	46.4	92.7	81.4	40.7	4.3	977.7	2.99
50.0	3.0	163.0	159.8	192.5	50.0	1.5	51.5	103.0	89.4	44.7	5.3	843.3	2.93
55.0	3.3	186.0	183.0	211.3	55.0	1.7	56.7	113.3	97.9	49.2	5.8	721.7	2.86
60.0	3.6	209.0	206.2	230.0	60.0	1.8	61.8	123.6	106.4	53.7	6.3	600.0	2.78

Log value of variables {[R-Cl]} Capacity Of Resin =264.5}

[R ₂ SO ₄] $\times 10^4$	[Cl ⁻] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - rx10 ² [R ₂ SO ₄]	log	logCl	logH	Log(R-Cl) _r	Z
20.6	80.4	26.8	184.6	-2.69	-2.09	-2.57	-1.73	-9.27
25.8	99.3	48.5	165.7	-2.59	-2.00	-2.31	-1.78	-8.11
30.9	118.1	70.2	146.9	-2.51	-1.93	-2.15	-1.83	-7.20
36.1	137.0	91.9	128.0	-2.44	-1.86	-2.04	-1.89	-6.40
41.2	155.9	113.6	109.1	-2.39	-1.81	-1.94	-1.96	-5.65
46.4	174.2	136.7	90.8	-2.33	-1.76	-1.86	-2.04	-4.93
51.5	192.5	159.8	72.5	-2.29	-1.72	-1.80	-2.14	-4.18
56.7	211.3	183.0	53.8	-2.25	-1.68	-1.74	-2.27	-3.34
61.8	230.0	206.2	35.0	-2.21	-1.64	-1.69	-2.46	-2.31

Table-5.5: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Ni-EDTA complex

[ML] initially taken (x) $\times 10^4 \text{M}$	[H ⁺] initially present in metal solution (a) $\times 10^4 \text{M}$	[H ⁺] found after equilibrium (b) $\times 10^4 \text{M}$	[H ⁺] remain (c) =b-a $\times 10^4 \text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in metal solution q ₁ $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in acid solution q ₂ $\times 10^4 \text{M}$	[SO ₄ ²⁻] present before equilibrium q=q ₁ +q ₂ $\times 10^4 \text{M}$	[Cl ⁻] liberated against SO ₄ ²⁻ (Q)= 2 x q $\times 10^4 \text{M}$	[Cl ⁻] remain r =p-Q $\times 10^4 \text{M}$	[R ₂ NiEDTA] =1/2of remain [Cl ⁻] y $\times 10^4 \text{M}$	[NiEDTA] _{ad} =x-y $\times 10^4 \text{M}$	λ	Log λ
20.0	37.2	49.5	12.3	90.0	20.0	18.6	38.6	63.2	26.8	13.4	6.6	203	2.31
25.0	46.5	58.8	12.3	121.3	25.0	23.3	48.3	89.5	31.8	15.9	9.1	180.3	2.26
30.0	55.8	68.1	12.3	152.5	30.0	27.9	57.9	115.8	36.7	18.4	11.6	157.5	2.20
35.0	65.1	77.1	12.0	174.6	35.0	32.6	67.6	134.9	39.7	19.9	15.1	136.0	2.13
40.0	74.4	86.0	11.6	196.7	40.0	37.2	77.2	154.0	42.7	21.4	18.6	114.4	2.06
45.0	83.7	93.8	10.1	215.4	45.0	41.9	86.9	173.5	41.9	20.9	24.1	92.0	1.96
50.0	93.0	101.5	8.5	234.0	50.0	46.5	96.5	193.0	41.0	20.5	29.5	69.5	1.84
55.0	102.3	109.3	7.0	245.5	55.0	51.2	106.2	212.0	33.5	16.8	38.3	48.6	1.69
60.0	111.6	117.0	5.4	257.0	60.0	55.8	115.8	231.0	26.0	13.0	47.0	27.6	1.44

Log value of variables {[R-Cl]}_{capacity of resin} =264.5}

[R ₂ SO ₄] $\times 10^4$	[Cl] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - rx10 ²	log [R ₂ SO ₄]	logCl	logH	Log(R-Cl) _r	Z
38.6	90.0	12.3	175.0	-2.41	-2.05	-2.91	-1.76	-9.39
48.3	121.3	12.3	143.8	-2.32	-1.92	-2.91	-1.84	-8.43
57.9	152.5	12.3	112.5	-2.24	-1.82	-2.91	-1.95	-7.53
67.6	174.6	12.0	90.4	-2.17	-1.76	-2.92	-2.04	-6.87
77.2	196.7	11.6	68.3	-2.11	-1.71	-2.94	-2.17	-6.15
86.9	215.4	10.1	49.7	-2.06	-1.67	-3.00	-2.30	-5.51
96.5	234.0	8.5	31.0	-2.02	-1.63	-3.07	-2.51	-4.65
106.2	245.5	7.0	19.5	-1.97	-1.61	-3.16	-2.71	-3.89
115.8	257.0	5.4	8.0	-1.94	-1.59	-3.27	-3.10	-2.44

Table-5.6: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Co-EDTA complex

[ML] initially taken (x) $\times 10^4 \text{M}$	[H ⁺] initially present in metal solution (a) $\times 10^4 \text{M}$	[H ⁺] found after equilibrium (b) $\times 10^4 \text{M}$	[H ⁺] remain (c) $=b-a$ $\times 10^4 \text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in metal solution q_1 $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in acid solution q_2 $\times 10^4 \text{M}$	[SO ₄ ²⁻] present before equilibrium $q=q_1+q_2$ $\times 10^4 \text{M}$	[Cl ⁻] liberated against SO ₄ ²⁻ (Q)= $2 \times q$ $\times 10^4 \text{M}$	[Cl ⁻] remain r =p-Q $\times 10^4 \text{M}$	[R ₂ CoEDTA] =1/2of remain [Cl ⁻] $\times 10^4 \text{M}$	[CoEDTA] _{aq} =x-y $\times 10^4 \text{M}$	λ	Log λ
20.0	40.6	80.1	39.5	105.1	20.0	20.3	40.3	80.6	24.5	12.2	7.8	158	2.20
25.0	50.3	91.3	41.0	133.8	25.0	25.2	50.2	100.3	33.5	16.7	8.3	199.5	2.30
30.0	60.0	102.5	42.5	162.5	30.0	30.0	60.0	120.0	42.4	21.2	8.8	240.9	2.38
35.0	70.6	113.9	43.3	181.7	35.0	35.3	70.3	140.6	40.6	20.3	14.7	167.6	2.22
40.0	81.2	125.2	44.0	200.9	40.0	40.6	80.6	161.2	38.8	19.4	20.6	94.2	1.97
45.0	91.4	132.9	41.5	213.0	45.0	45.7	90.7	181.3	31.3	15.7	29.4	62.6	1.80
50.0	101.5	140.5	39.0	225.1	50.0	50.7	100.7	201.4	23.7	11.9	38.1	31	1.49
55.0	111.7	147.9	36.2	243.1	55.0	55.8	110.8	221.6	21.5	10.8	44.3	25.0	1.40
60.0	121.8	155.2	33.4	261.0	60.0	60.9	120.9	241.8	19.2	9.6	50.4	19	1.28

Log value of variables {[R-CL]_{capacity of resin} =264.5}

[R ₂ SO ₄] $\times 10^4$	[Cl ⁻] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - rx10 ²	log [R ₂ SO ₄]	logCl	logH	Log(R-Cl) _r	Z
40.3	105.1	39.5	159.9	-2.39	-1.98	-2.40	-1.80	-7.9
50.2	133.8	41.0	131.2	-2.30	-1.87	-2.39	-1.88	-7.0
60.0	162.5	42.5	102.6	-2.22	-1.79	-2.37	-1.99	-6.2
70.3	181.7	43.3	83.3	-2.15	-1.74	-2.36	-2.08	-5.5
80.6	200.9	44.0	64.1	-2.09	-1.70	-2.36	-2.19	-4.8
90.7	213.0	41.5	52.0	-2.04	-1.67	-2.38	-2.28	-4.4
100.7	225.1	39.0	39.9	-2.00	-1.65	-2.41	-2.40	-3.8
110.8	243.1	36.2	22.0	-1.96	-1.61	-2.44	-2.66	-2.7
120.9	261.0	33.5	4.0	-1.92	-1.58	-2.48	-3.40	0.4

Table-5.7: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Cu-EDTA complex

[ML] initially taken (x) $\times 10^4 \text{M}$	[H ⁺] initially present in metal solution (a) $\times 10^4 \text{M}$	[H ⁺] found after equilibrium (b) $\times 10^4 \text{M}$	[H ⁺] remain (c) $=b-a$ $\times 10^4 \text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in metal solution q_1 $\times 10^4 \text{M}$	[SO ₄ ²⁻] present in acid solution q_2 $\times 10^4 \text{M}$	[SO ₄ ²⁻] present before equilibrium $q=q_1+q_2$ $\times 10^4 \text{M}$	[Cl ⁻] liberate d against SO ₄ ²⁻ (Q)= 2 x q $\times 10^4 \text{M}$	[Cl ⁻] remain r =p-Q $\times 10^4 \text{M}$	[R ₂ CuEDTA] =1/2 of remain [Cl ⁻] y $\times 10^4 \text{M}$	[CuEDTA] _{aq} =x-y $\times 10^4 \text{M}$	λ	Log λ
20.0	39.0	79.2	40.2	125.0	20	19.5	39.5	79.0	46.0	23.0	-	-	-
25.0	48.8	96.0	47.3	150.1	25	24.4	49.4	98.8	51.3	25.6	-	-	-
30.0	58.5	112.8	54.3	175.2	30	29.2	59.2	118.5	56.5	28.2	1.75	1042.8	3.02
35.0	68.3	133.2	65.0	200.4	35	34.1	69.1	138.3	62.0	31.0	4.00	791.4	2.90
40.0	78.0	153.6	75.6	225.5	40	39.0	79.0	158.0	67.5	33.7	6.25	540.0	2.73
45.0	87.8	187.5	99.7	245.3	45	43.9	88.9	177.8	67.5	33.7	11.30	373.9	2.57
50.0	97.5	221.3	123.8	265.0	50	48.7	98.7	197.5	67.5	33.7	16.25	207.7	2.32

Log value of variables {[R-Cl]}_{capacity of resin} =264.5}

[R ₂ SO ₄] $\times 10^4$	[Cl] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - rx10 ²	log [R ₂ SO ₄]	logCl	logH	Log(R-Cl) _r	Z
39.5	125.0	40.2	140.0	-2.40	-1.90	-2.40	-1.85	-7.39
49.4	150.0	47.3	115.0	-2.31	-1.82	-2.33	-1.94	-6.50
59.3	175.0	54.3	90.0	-2.23	-1.76	-2.27	-2.05	-5.60
69.1	200.0	65.0	65.0	-2.16	-1.70	-2.19	-2.19	-4.58
79.0	225.0	75.6	40.0	-2.10	-1.65	-2.12	-2.40	-3.34
88.9	244.5	99.7	20.5	-2.05	-1.61	-2.00	-2.69	-1.75
98.8	264.0	123.8	1.00	-2.01	-1.58	-1.91	-4.00	3.87

Table-5.8: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Pb-EDTA complex

[ML] initially taken (x) $\times 10^4 \text{M}$	[H+] initially present in metal solution (a) $\times 10^4 \text{M}$	[H+] found after equilibrium (b) $\times 10^4 \text{M}$	[H ⁺] remain (c) $=b-a$ $\times 10^4 \text{M}$	[Cl ⁻] found after equilibrium (p) $\times 10^4 \text{M}$	[NO ₃] present in metal solution q_1 $\times 10^4 \text{M}$	[NO ₃] present in acid solution q_2 $\times 10^4 \text{M}$	[NO ₃] present before equilibrium $q=q_1+q_2$ $\times 10^4 \text{M}$	[Cl ⁻] liberate d against NO ₃ ⁻ (Q)= $\times 10^4 \text{M}$	[Cl ⁻] remain r = p-Q $\times 10^4 \text{M}$	[R ₂ PbEDTA] = 1/2 of remain [Cl ⁻] $\times 10^4 \text{M}$	[PbEDTA] _{aq} = x-y $\times 10^4 \text{M}$	λ	Log λ
20.0	25.2	48.0	22.8	80.2	20.0	25.2	45.2	45.2	35.0	17.5	2.5	700.0	2.85
25.0	31.5	62.2	30.7	93.3	25.0	31.5	56.5	56.5	36.8	18.4	6.6	439.5	2.64
30.0	37.8	76.3	38.5	106.3	30.0	37.8	67.8	67.8	38.5	19.2	10.7	179.0	2.25
35.0	44.1	90.4	58.5	113.2	35.0	44.1	79.1	79.1	34.1	17.0	18.0	99.0	2.00
40.0	50.4	104.5	78.4	120.0	40.0	50.4	90.4	90.4	29.6	14.8	25.2	19.0	1.28
45.0	56.7	123.0	78.4	131.1	45.0	56.7	101.7	101.7	29.4	14.7	30.4	15.8	1.20
50.0	63.0	141.4	78.4	142.1	50.0	63.0	113.0	113.0	29.1	14.5	35.5	12.6	1.10
55.0	69.4	159.9	90.5	151.1	55.0	69.4	124.4	124.4	26.7	13.3	41.7	18.9	1.28
60.0	75.8	178.3	102.5	160.0	60.0	75.8	135.8	135.8	24.2	12.1	47.9	25.2	1.40

Log value of variables { [R-Cl] capacity of resin = 264.5 }

[R ₂ SO ₄] $\times 10^4$	[Cl ⁻] $\times 10^4$	[H] $\times 10^4$	(R-Cl) _r = (R-Cl) - rx10 ²	log [R ₂ SO ₄]	logCl	logH	Log(R-Cl) _r	Z
45.2	80.2	22.8	184.8	-2.34	-2.10	-2.64	-1.73	-9.08
56.5	93.3	30.7	171.8	-2.25	-2.03	-2.51	-1.77	-8.34
67.8	106.3	38.5	158.7	-2.17	-1.97	-2.41	-1.80	-7.69
79.1	113.2	58.5	151.9	-2.10	-1.95	-2.23	-1.82	-7.08
90.4	120.0	78.4	145.0	-2.04	-1.92	-2.11	-1.84	-6.58
101.7	131.1	78.4	134.0	-1.99	-1.88	-2.11	-1.87	-6.24
113.0	142.1	78.4	122.9	-1.95	-1.85	-2.11	-1.91	-5.91
124.4	151.1	90.5	114.0	-1.91	-1.82	-2.04	-1.94	-5.50

135.8	160.0	102.5	105.0	-1.87	-1.80	-1.99	-1.98	-5.11
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Table-5.9: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of Al-EDTA complex

[ML] initially taken (x) $\times 10^4 \text{M}$	[H+] initially present in metal solution (a) $\times 10^4 \text{M}$	[H+] found after equilibrium (b) $\times 10^4 \text{M}$	[H ⁺] remain (c) $=b-a$ $\times 10^4 \text{M}$	[Cl] found after equilibrium (b) $\times 10^4 \text{M}$	[NO ₃] present in metal solution q_1 $\times 10^4 \text{M}$	[NO ₃] present in acid solution q_2 $\times 10^4 \text{M}$	[NO ₃] present before equilibrium $q=q_1+q_2$ $\times 10^4 \text{M}$	[Cl] liberate d against NO_3^- (Q)= $\times 10^4 \text{M}$	[Cl] remain $r=p-Q$ $\times 10^4 \text{M}$	[RAIEDTA] $=1/2$ of remain [Cl] $\times 10^4 \text{M}$	[AIEDTA] $=x-y$ $\times 10^4 \text{M}$	λ	Log λ
20.0	35.5	60.0	24.5	111.0	60.0	35.5	95.5	95.5	15.5	15.5	4.5	344.4	2.5
25.0	44.4	70.5	26.1	135.8	75.0	44.4	119.4	119.4	16.4	16.4	8.6	239.9	2.4
30.0	53.2	81.0	27.7	160.5	90.0	53.2	143.2	143.2	17.2	17.2	12.7	135.3	2.1
35.0	62.1	91.3	29.1	185.4	105.0	62.1	167.1	167.1	18.2	18.2	16.8	113.8	2.1
40.0	71.0	101.5	30.5	210.2	120.0	71.0	191.0	191.0	19.2	19.2	20.8	92.3	2.0
45.0	79.9	110.9	31.0	235.4	135.0	79.9	214.9	214.9	20.5	20.5	24.5	84.6	1.9
50.0	88.7	120.2	31.4	260.5	150.0	88.7	238.7	238.7	21.7	21.7	28.2	76.9	1.9
55.0	97.6	129.7	31.5	260.5	165.0	97.7	262.7	262.7	-	-	-	-	-
60.0	106.5	139.1	31.6	260.5	180.0	106.6	286.6	286.6	-	-	-	-	-

Log value of variables {[R-Cl]}_{capacity of resin} =264.5}

[RNO ₃] $\times 10^4$	[Cl] $\times 10^4$	$\frac{(R-Cl)_r}{(R-Cl) - r} \times 10^2$	log [RNO ₃]	logCl	Log(R-Cl) _r	Z
95.5	111.0	154.0	-2.02	-1.95	-1.81	-2.59
119.4	135.8	129.3	-1.92	-1.87	-1.89	-1.84
143.3	160.5	104.5	-1.84	-1.79	-1.98	-1.10
167.1	185.4	79.7	-1.78	-1.73	-2.10	-0.31
191.0	210.2	54.8	-1.72	-1.68	-2.26	0.62
214.9	235.4	29.7	-1.67	-1.63	-2.53	1.93
238.8	260.5	4.5	-1.62	-1.58	-3.35	5.43

Table-5.10: Concentration of various equilibrium species in aqueous and resin phases and distribution coefficient of La-EDTA complex

[ML] initially taken (x) $\times 10^4 M$	[H ⁺] initially present in metal solution (a) $\times 10^4 M$	[H ⁺] found after equilibri um (b) $\times 10^4 M$	[H ⁺] remain (c) $=b-a$ $\times 10^4 M$	[Cl ⁻] found after equilibrium (p) $\times 10^4 M$	[NO ₃] present in metal solution q_1 $\times 10^4 M$	[NO ₃] present in acid solution q_2 $\times 10^4 M$	[NO ₃] present before equilibrium $q=q_1+q_2$ $\times 10^4 M$	[Cl ⁻] liberate d against NO ₃ ⁻ (Q)= $\times 10^4 M$	[Cl ⁻] remain r = p-Q $\times 10^4 M$	[RLaEDTA] = 1/2 of remain [Cl ⁻] y $\times 10^4 M$	[LaEDTA] _{aq} = x-y $\times 10^4 M$	λ	Log λ
20.0	6.2	35	28.8	65	60	6.2	66.2	66.1	-	-	-	-	-
25.0	7.8	38.8	31.0	82.6	75.0	7.8	82.8	82.7	-	-	-	-	-
30.0	9.3	42.5	33.2	100.2	90	9.3	99.3	99.3	0.9	0.9	29.1	3.1	0.5
35.0	10.9	46.3	35.5	125.5	105.0	10.9	115.9	115.9	9.7	9.7	25.4	44.2	1.6
40.0	12.4	50.1	37.7	150.8	120	12.4	132.4	132.4	18.4	18.4	21.6	85.2	1.9
45.0	14.0	52.7	38.7	176.0	135.0	14.0	149.0	149.0	27.0	27.0	18.0	166.2	2.2
50.0	15.5	55.2	39.7	201.1	150	15.5	165.5	165.5	35.6	35.6	14.4	247.2	2.4
55.0	17.1	57.6	40.6	225.6	165.0	17.1	182.1	182.1	43.5	43.5	11.5	422.5	2.6
60.0	18.6	60	41.4	250	180	18.6	198.6	198.6	51.4	51.4	8.6	597.7	2.8

Log value of variables {[R-Cl]_r capacity of resin = 264.5}

[RNO ₃] $\times 10^4$	[Cl] $\times 10^4$	(R-Cl) _r = (R-Cl) - r $\times 10^2$	log [RNO ₃]	logCl	Log(R-Cl) _r	Z
-	-	-	-	-	-	-
-	-	-	-	-	-	-
99.3	100.0	165.0	-2.00	-2.00	-1.78	-2.87
115.9	125.4	139.6	-1.94	-1.90	-1.86	-2.12
132.4	150.8	114.2	-1.88	-1.82	-1.94	-1.40
149.0	176.0	89.1	-1.83	-1.75	-2.05	-0.64
165.5	201.1	63.9	-1.78	-1.70	-2.19	0.21
182.1	225.6	39.5	-1.74	-1.65	-2.40	1.29
198.6	250.0	15.0	-1.70	-1.60	-2.82	3.19

Fig. 5.1 Plot of $\text{Log } \lambda$ vs Z for $\text{Mg(II)}\text{-EDTA}$ system

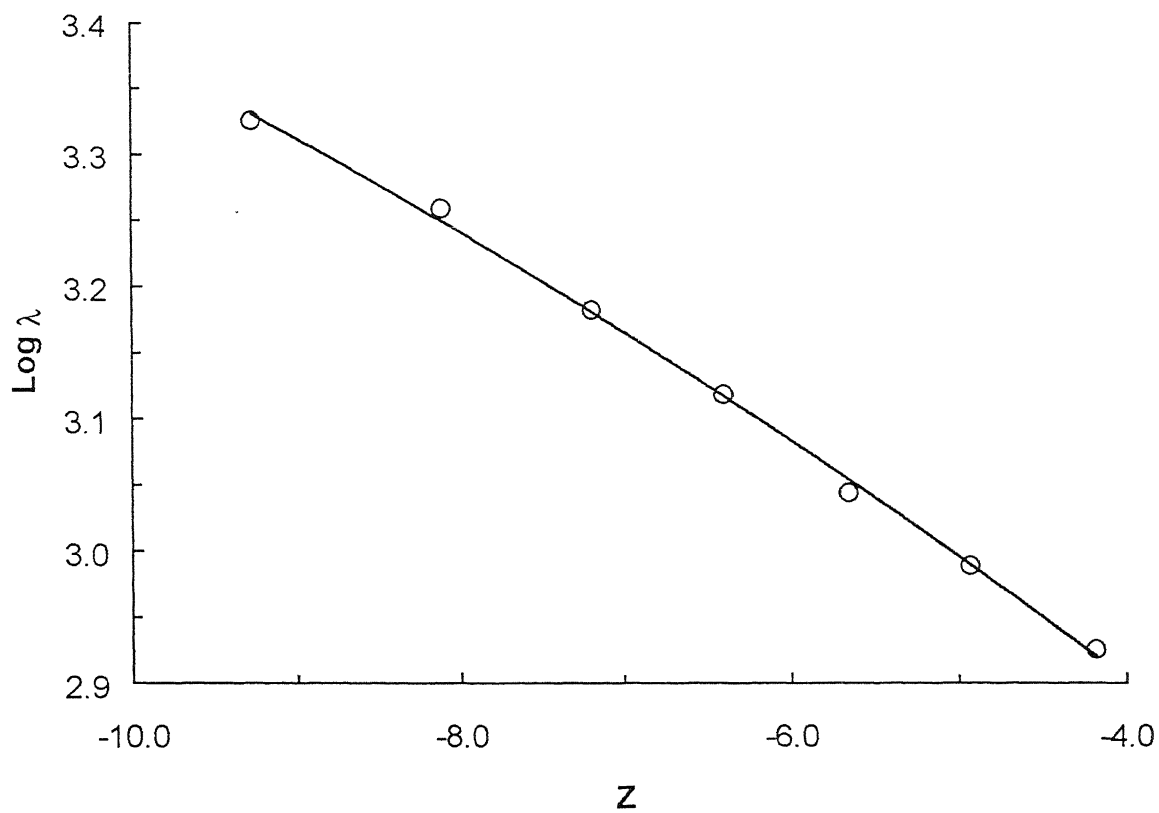


Fig. 5.2 Plot of $\text{Log } \lambda$ vs Z for $\text{Mn(II)}\text{-EDTA}$ system

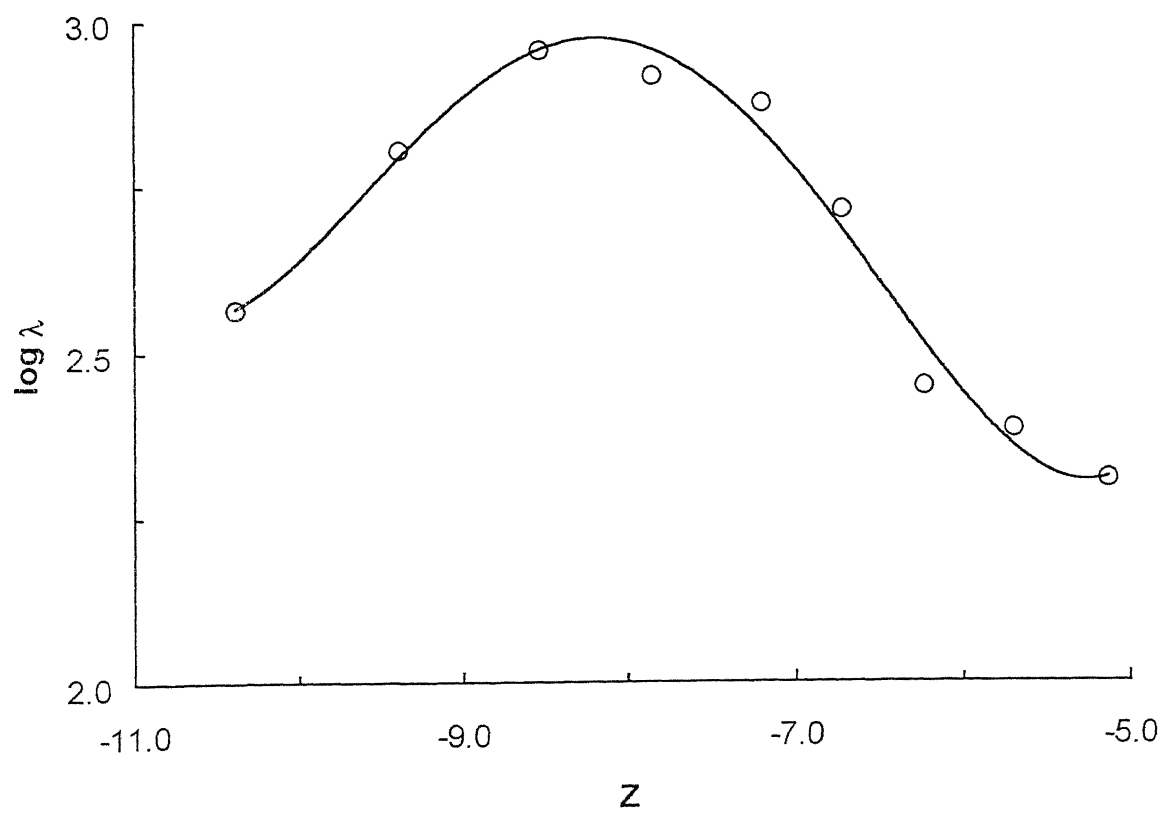


Fig. 5.3 Plot of $\text{Log } \lambda$ vs Z for Al(III)-EDTA system

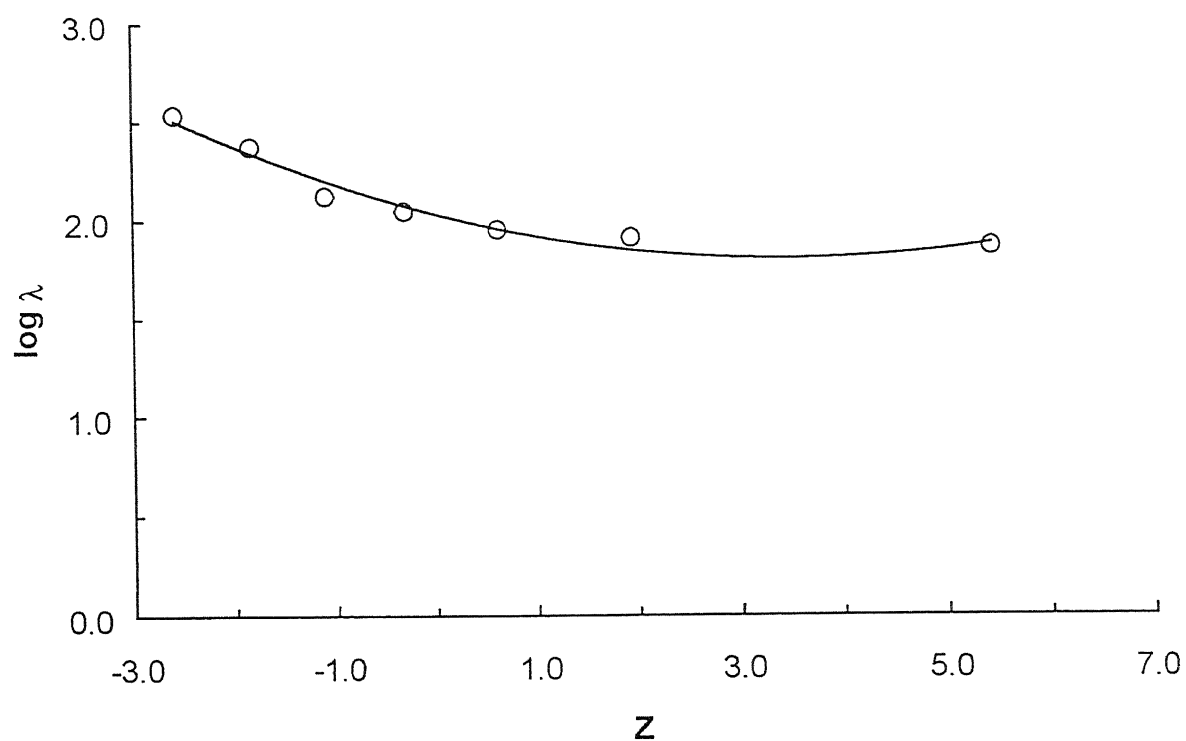


Fig. 5.4 Plot of $\text{Log } \lambda$ vs Z for Fe(III)-EDTA system

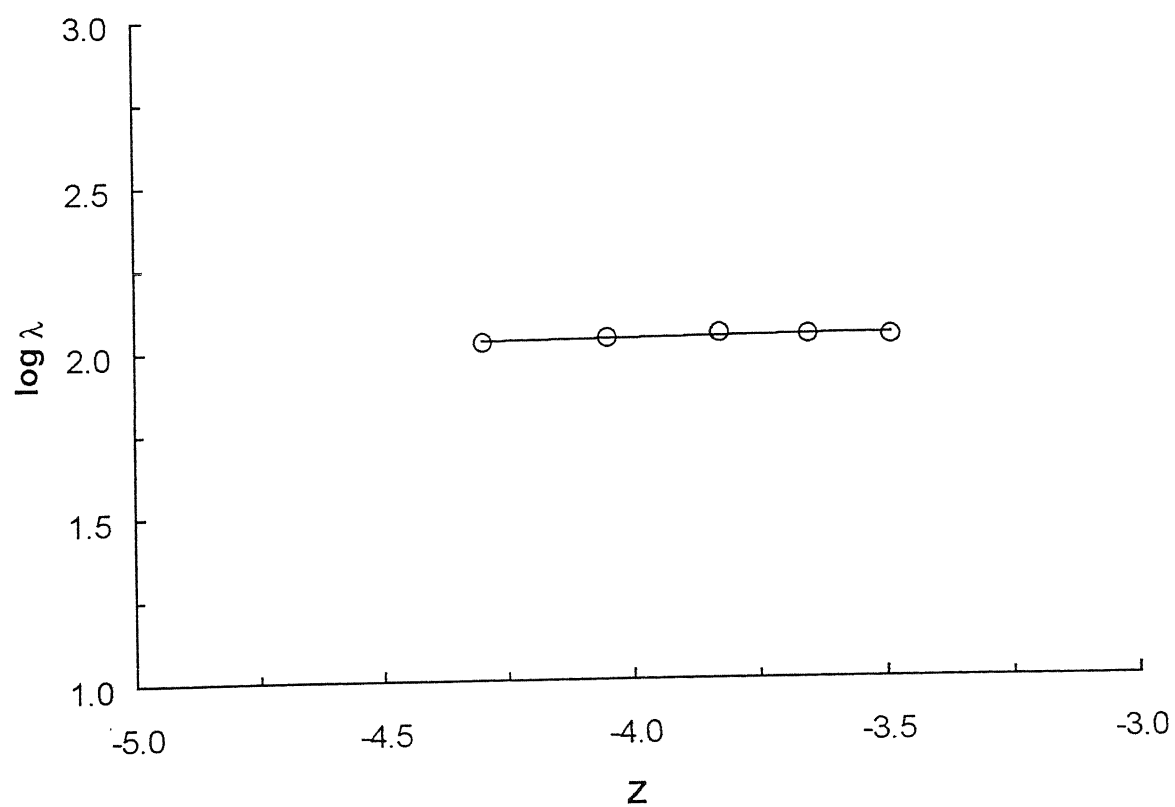


Fig. 5.5 Plot of $\text{Log } \lambda$ vs Z for Ni(II)-EDTA system

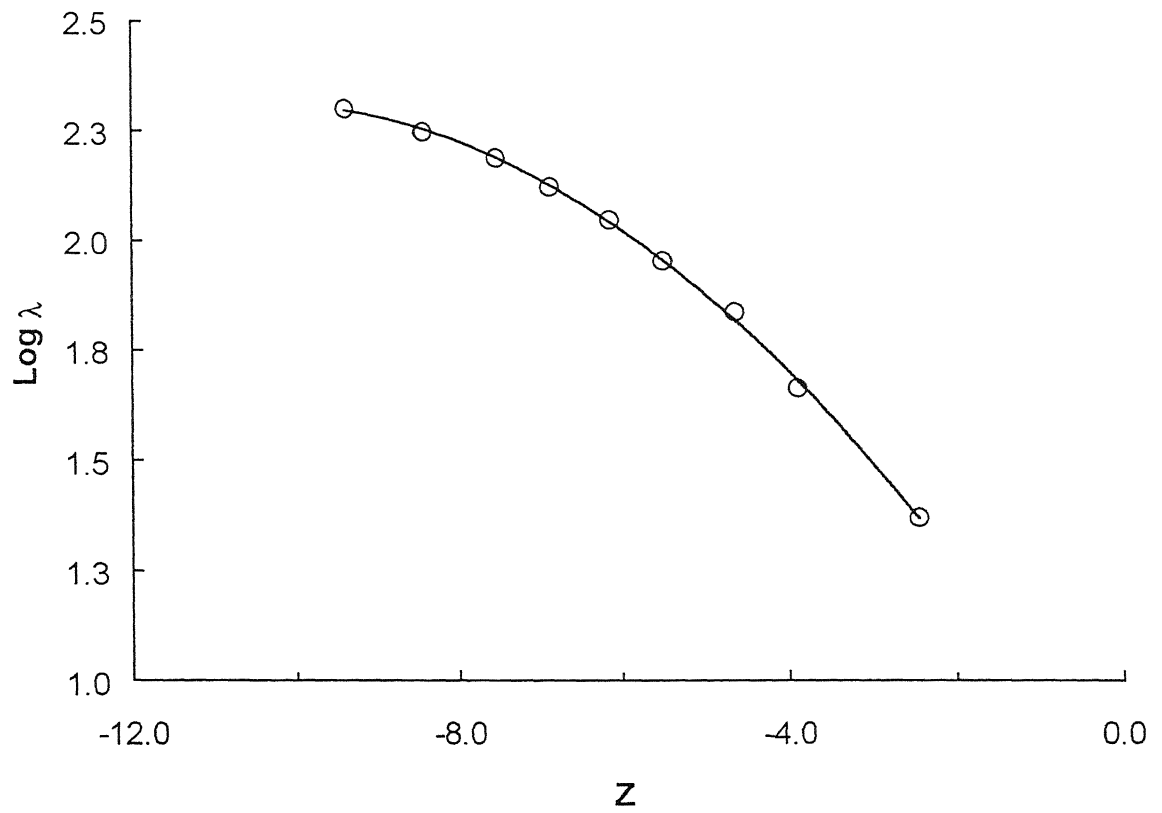


Fig. 5.6 Plot of $\text{Log } \lambda$ vs Z for Co(II)-EDTA system

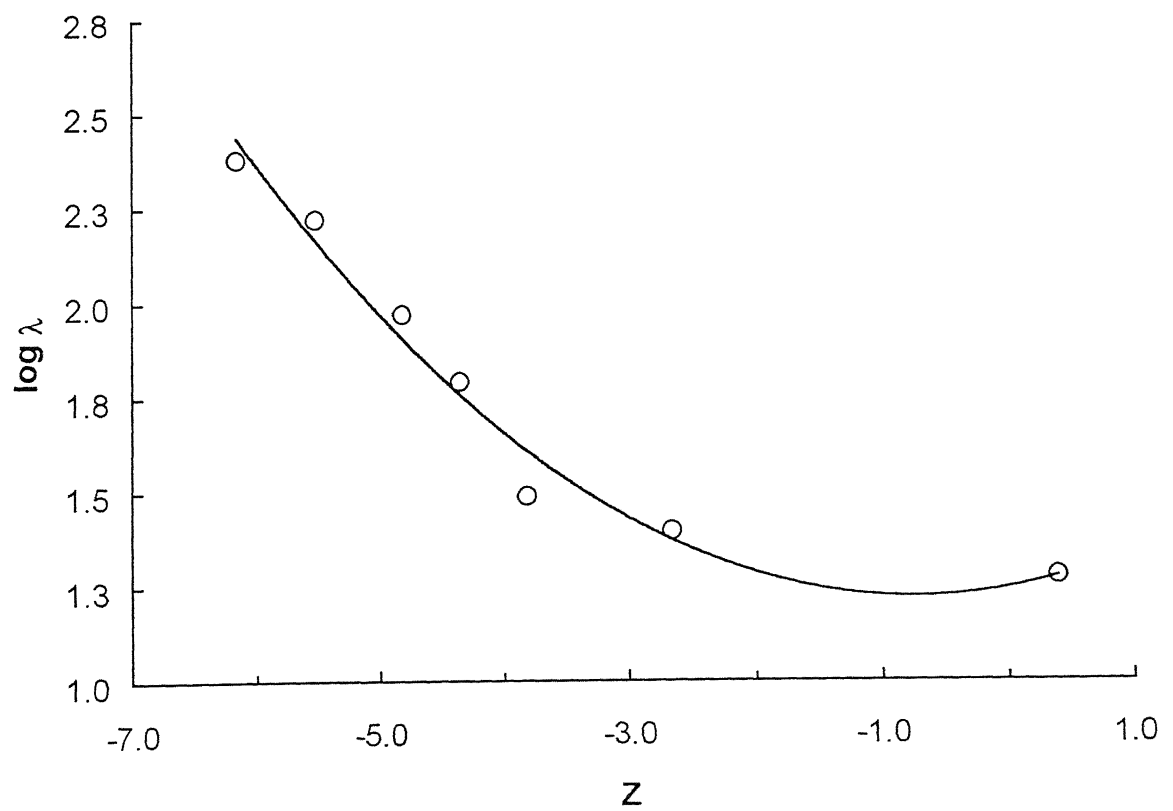


Fig. 5.7 Plot of $\text{Log } \lambda$ vs Z for Cu(II)-EDTA system

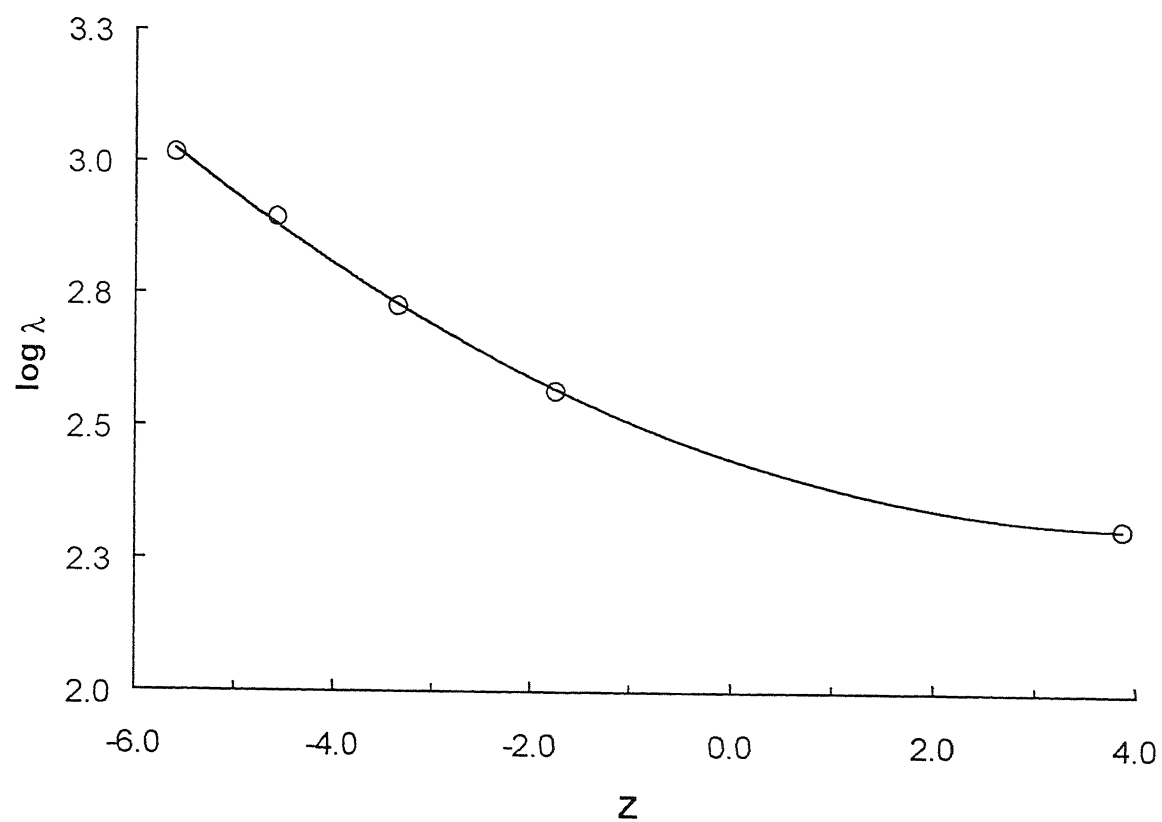


Fig. 5.8 Plot of $\text{Log } \lambda$ vs Z for Pb(II)-EDTA system

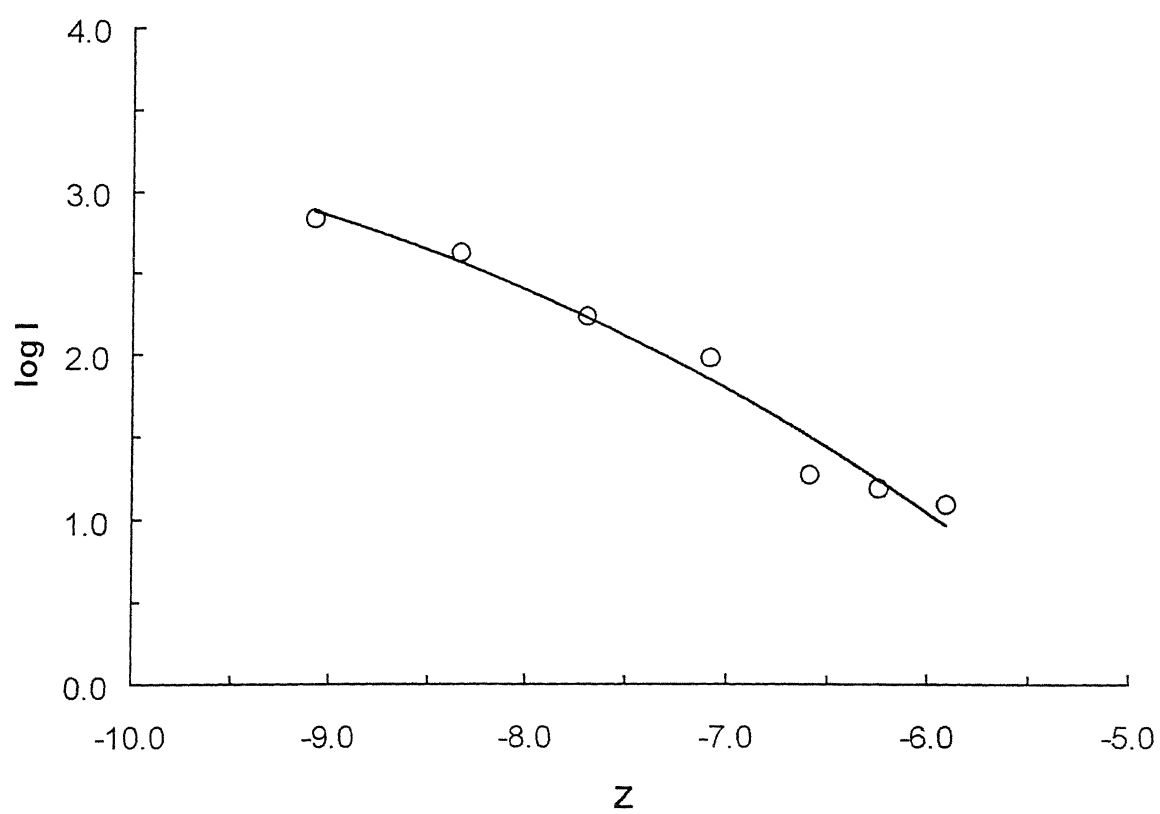


Fig. 5.9 Plot of $\text{Log } \lambda$ vs Z for Ca(II)-EDTA system

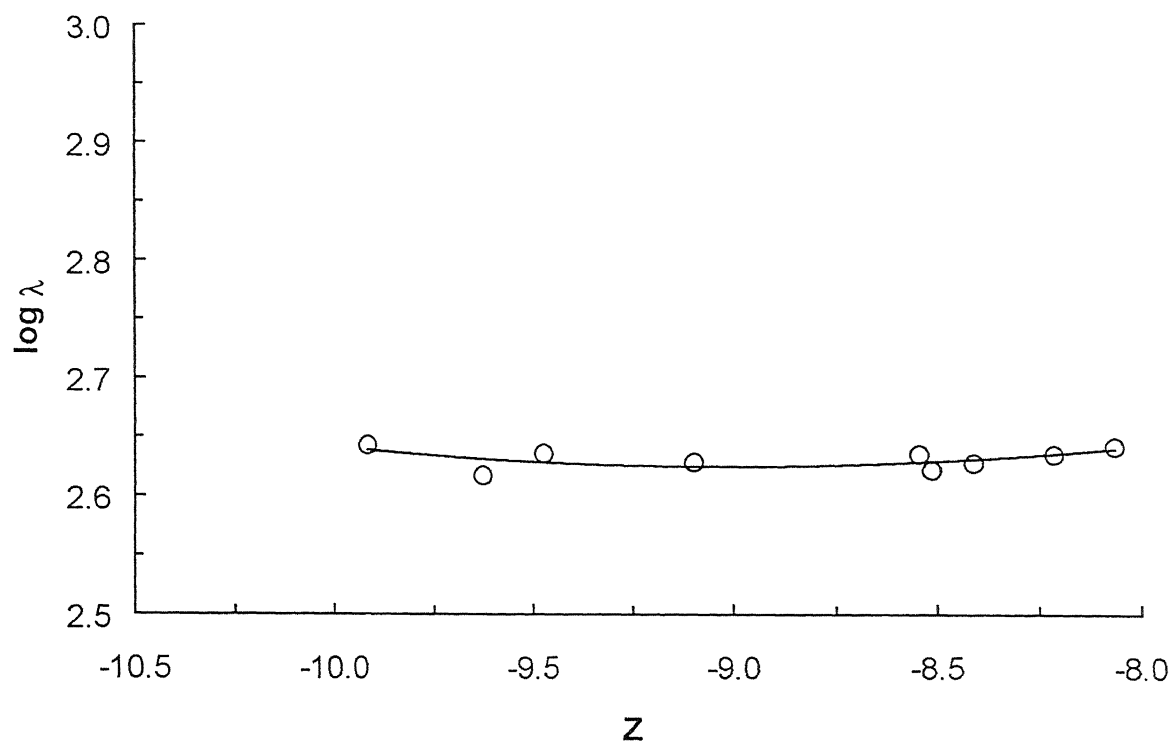
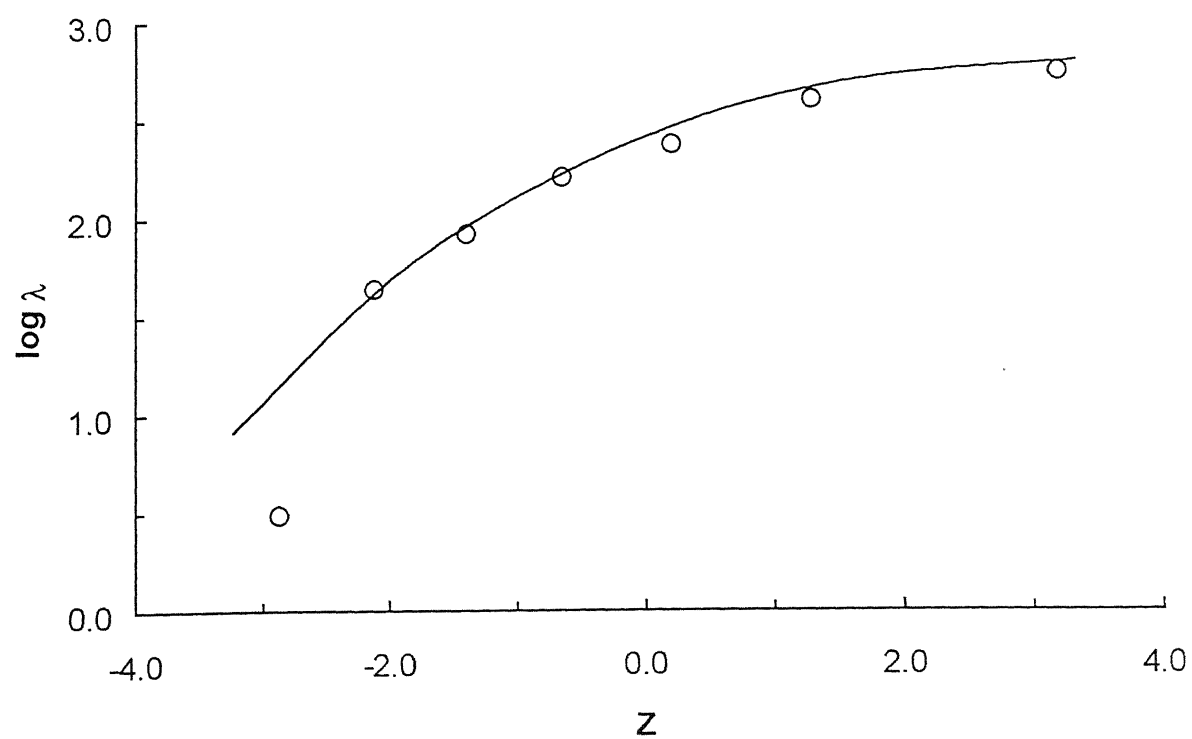


Fig. 5.10 Plot of $\text{Log } \lambda$ vs Z for La(II)-EDTA system



The various metal ions EDTA anionic species are exchanging less toward chloride at higher concentration, but dilute in solutions almost complete sorption can be achieved. It is in agreement with the common sorption tendencies, i.e. a maximum sorption could be possible if the concentration of sorbable species is kept less than 40% of the exchanger's capacity.

Table.5.11: Ion Exchange equilibrium constant of Metal ions

Metal ion	La(II)	Fe(II)	Mg(II)	Ni(II)	Co(II)	Cu(II)	Mn(II)	Pb(II)	Ca(II)	Al(III)
logK	2.45	2.11	2.46	0.70	1.25	1.52	3.19	12.84	4.03	2.04

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CHAPTER – 6

GENERAL DISCUSSION AND SUMMARY

The brief account of the work carried out is described in this chapter. The introductions of the research problems are presented in chapter 1 describing the salient features highlighting the important and manifold its applications (8,20). The associated characteristics properties of ion exchange materials of both anion and cation exchange resins are suitably exploited for investigating the selected systems (1,2,3,6). Resins of appropriate desired work have been used and their ion exchange capacities have been determined and accordingly the range of experiments were decided. Capacities data thus obtained are used to work out the experimental concentrations which were taken for equilibrium and dynamic column performances.(18,21). Chelating type exchanger (6,11) was prepared, i.e., using Amberlite IRA – 400 anion exchanger in the EDTA – form, which has been found to have a specific use. The observations encountered in these ion exchange investigations have been discussed by considering the affinity and swelling aspects of the resins, and the ion exchange effects on the species involved were concluded, and resulted were reported in respective chapters. Ion exchange study is important and is directly linked with the ionic nature and behaviour of the species presented in the solution and resin phases, as well as selectivity tendencies towards the exchanger used as synthetic resin may be possessing weakly acidic, strongly acidic and medium acidic (for cation exchanger) and weakly basic, strongly basic and medium basic (for anion exchanger) exchange nature. Both methodologies the batch equilibrium process and / or the column operation were applied using the sorption and elution technique. The results of batch method were used to have information's about the sorbability of the species present in the sorption, and were reported as percentage of loading (L%). The loading were evaluated from the distribution coefficient value of the concern species determined by batch equilibria. The column operation was performed to get the precise results in order to improve further the effectiveness of the practical work. Column results may be considered comparable with the chromatographic process (4,7,8,17).

The theoretical aspects and the different quantities related with the ion exchange equilibrium studies are given in chapter 2.

The studies of metal ions in constant acetic acid and varying NH_4OAc – OXAc media were presented in chapter 3 in the cationic and anionic ion exchange

characteristics of Mg(II), Mn(II), Al(III), Fe(II and III), Ni(II) and Zn(II) were carried out in the selected concentration range of these media. The resin Amberlite IR-120 (strongly basic and NH_4^+ form) and Amberlite IRA-400 (strongly acidic in Cl^- form) were selected for these investigation. The workable concentration range was between $3.00 \times 10^{-3} \text{ M}$ to $9.00 \times 10^{-3} \text{ M}$.

Table-6.1: Values of Distribution Coefficient (D) of $\text{NH}_4\text{OAc} - \text{OXAc}$ media
($\text{AcOH} = 0.25\text{M}$) of Amberlite IR- 120 (NH_4^+ – form)

Concentration of $[\text{OX}] \times 10^3$	Distribution Coefficient of Metal Ion $[3.0 \times 10^3]$						
	Mg(II)	Al(II)*	Mn(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)**
4.00	400.0	186.0	130.7	1363.4	552.2	408.4	400.0
4.25	310.0	200.0	122.5	1283.8	510.7	365.3	355.9
4.50	233.3	216.6	114.3	1204.3	469.2	328.9	310.9
4.75	187.0	233.3	110.5	1137.6	413.9	297.8	272.5
5.00	150.0	254.1	100.0	1071.8	358.7	271.0	233.3
5.25	119.0	275.0	96.5	1019.7	332.5	247.8	205.5
5.50	106.8	301.7	88.5	967.6	306.3	227.4	177.7
5.75	78.0	328.5	80.7	922.3	276.5	209.6	163.8
6.00	66.6	364.2	71.4	877.1	246.8	193.8	150.0
6.25	54.0	400.0	68.1	838.5	224.6	179.8	132.1
6.50	41.5	450.0	64.9	800.9	202.4	167.3	114.2
6.75	84.0	500.0	53.8	768.5	185.2	156.1	257.1
7.00	150.0	575.0	42.8	737.9	168.1	146.0	400.0
7.25	257.1	650.0	36.8	709.8	154.0	136.9	P
7.50	400.0	575.0	30.4	681.7	140.7	128.6	P
7.75	P	500.0	30.4	656.7	128.6	121.1	P
8.00	P	450.0	30.4	631.7	116.5	114.2	P
8.25	P	364.2	30.4	610.6	108.5	108.0	P
8.50	P	328.5	30.4	589.6	100.0	102.2	P
8.75	P	301.7	30.4	569.8	100.0	96.9	P
9.00	P	275.0	30.4	550.6	100.0	92.0	P

P = precipitate

* = Reading taken from 3.0×10^{-3} up to $13 \times 10^{-3} \text{ M}$ of $[\text{OX}]$ concentration see in discussion

** = Reading taken from $3.25 \times 10^{-3} \text{ M}$ of $[\text{OX}]$ concentration see in discussion

The distribution measurement of cation exchange studies were used for determining the stability constant of various metal complexations equilibrium systems by application of Shubert's Method. While Froneous Method was employed for such evaluations of anion exchange studies. The results were discussed that these mixed media in the constant acetic acid are promising and valuable because of new impacts found due to these effects in the sorption behaviours of studied metal ions. Mg(II), Ni(II) and Fe(II and III) have shown a decreasing order in which the nature in case of Mn(II) is found a straight line while other metal ions have just shown curved line behaviours. The behaviors of Mg(II), Zn(II) and Al(III) have been found unusual or unique. A unusual sorption trend was observed in case of Mg(II) (16) showing the highest sorption observed at 4.00×10^{-3} M equimolar NH_4OAc - OXAc mixture (at constant 0.25 M AcOH) solution with a D-value = 400.0. Then a gradual decrease was observed up to 6.25×10^{-3} M equimolar mixture solution, and again the D-value started increasing up to 7.50×10^{-3} M equimolar mixture solution giving the same observed D-value = 400.0. The experiments of Mg(II) beyond above mentioned concentration range (lower and higher) could not be performed due to formation of precipitate.

Zn(II) have also shown to some extent the relative similar behaviour like Mg(II)(9). But this may not be considered exactly like Mg(II) i.e. only at the last three concentrations before the precipitate formation appear an increase in its D-values has been observed.

But the case of Al(III) has been found just reverse of the Mg(II) and may be considered abnormal as indicated by the observed results. A gradual enhancement in the D-value has been observed with the increase of equimolar NH_4OAc - OXAc mixture solutions. This finding may be described as a very rare and unusual sorption nature shown by the Al(III) i.e. instead by complexation D-values should decrease these are found increasing up to D-value = 650.0 and after this the decreasing trend has been observed i.e. equal to initial D-value data of 114.8.

The anion exchange studies were performed in the media as were taken for cation exchange investigations.

Table-6.2: Values of Distribution Coefficient (D) of NH₄OAc – OXAc media
(AcOH = 0.25M) of Amberlite IRA - 400 (Cl⁻ - form)

Concentration of [OX] x 10 ³	Distribution Coefficient of Metal Ion						
	Mg(II)	Al(II)*	Mn(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)**
4.00	25.0	53.9	76.5	7.3	8.3	25.0	25.0
4.25	33.9	50.0	82.5	7.8	10.9	27.5	28.5
4.50	42.8	46.4	88.5	8.3	13.5	30.4	32.1
4.75	54.7	42.8	94.45	8.8	16.3	33.0	37.1
5.00	66.6	39.5	100.0	9.4	19.2	35.7	42.8
5.25	80.0	36.3	106.2	10.1	22.3	39.6	49.5
5.50	93.5	33.6	112.7	10.7	25.5	43.5	56.2
5.75	121.7	30.4	126.3	11.1	29.0	46.7	61.2
6.00	150.0	27.9	140.0	11.5	32.6	50.0	66.6
6.25	195.0	25.0	147.1	12.1	36.5	53.9	77.0
6.50	240.0	22.5	154.2	12.8	40.5	57.9	87.5
6.75	118.9	20.0	193.7	13.1	45.0	62.2	38.8
7.00	66.6	17.65	233.3	13.5	49.5	66.6	25.0
7.25	39.5	15.3	280.9	13.8	54.4	71.5	P
7.50	25.0	17.65	328.5	14.5	59.4	76.5	P
7.75	P	20.0	328.5	15.1	65.2	82.0	P
8.00	P	22.5	328.5	15.8	71.0	87.5	P
8.25	P	25.0	328.5	16.4	77.65	93.7	P
8.50	P	27.9	328.5	17.1	84.3	100.0	P
8.75	P	30.4	328.5	17.6	100	107.6	P
9.00	P	33.6	328.5	18.1	100	115.2	p

P = precipitate

* = reading taken from 3.0 X 10⁻³ up to 13 X 10⁻³M of [OX] concentration see in discussion

** = reading taken from 3.25 X 10⁻³M of [OX] concentration it shows in discussion

Metal ions Mn(II), Fe(II and III) and Ni(II) have shown a gradual increase of D-values clearly indicating the involvement of these ions in the complexation activities leading to their gradual more and more uptake by the anion exchanger. The D-values plots of Mn(II), Fe(II) and Ni(II) were found to have curved nature while that of Fe(II) a straight line, but Mg(II) has shown a different and unique sorption pattern, i.e. , the sorption has not followed the common trend. The lowest sorption was observed at 4.00 x 10⁻³ M equimolar NH₄OAc-OXAc mixture (at constant 0.25 M AcOH) solution with a D-value = 25.0. A gradual increase has been observed to a highest at

6.25×10^{-3} equimolar mixture solution and then again the D-values have decreasing tendency up to 7.50×10^{-3} M equimolar mixture solution with same observed D-value=25.0. Similarly for these experiments beyond the selected concentration range of the media could not be performed due to precipitation.

The result of the Zn(II) systems are all together like Mg(II)(9) and are comparable with a little variation in the observations.

The complexation tendency of Al(III) with oxalate (14,15) and/or acetate (13,22) may be considered to be effectively operating in such way that the gross anionic species formation is gradually decreasing therefore observed D-values are falling gradually till 8.00×10^{-3} M equimolar mixture solutions, but beyond this limit or at higher concentration the decreasing trend has changed to an increasing pattern which has probably been resulted due to dominance of strong complexation and subsequent more formation anionic species at high concentration media. The complexation equilibrium involving oxalate appears relatively more dominating and effective as well as the acetate is playing a vital role especially for enhancing the solubility of oxalate species(17,18). Also it may not be incorrect to presume that in the investigated range of equimolar mixture solution media, neither the pure metal oxalate species nor the pure metal acetate species which have been formed are carrying the mixed ligand complexing nature involving both these anion to present in the coordination sphere is of the central metal ion. This mixed complexation appears not affecting the charge on the respective species because of the symmetric arrangements therefore the effecting distribution of the metal with respect to charge is not changing contrary to other factors like overall size of the metal complex species has definitely differed and subsequently affecting overall metal ion distribution resulting in the variation of evaluated D-value.

Though the ion exchange method has still not been extended to be applied to the mixed ligand system even then present investigations have been used to evaluate the stability or formation constant of the various studied systems considering the oxalate concentration and for this purpose the practical effect of acetate have been ignored therefore the 'K' and β values thus obtained are related to acetate as in other studies were ClO_4^- , NO_3^- or Cl^- etc. is used either as maintaining the ionic strength of the medium or as co-anion of the metal. Attempts have also

been made to calculate in the same way the 'K' and β values with respect to acetate and ignoring the effects of oxalate. Results were compared and discussed in the light of sorbable tendencies considering the mixed ligand effect.

Table:6.3: The calculation of the equilibrium formation constants of the studied metal ions with respect to complexation with oxalate

Metal Ion	D_o	Log k_1	Log β_2	Log β_3
Mg (II)	24097	4.8	6.3	9.6
Al (III)	10288	3.7	6.0	8.0
Mn (II)	243	2.8	5.3	7.8
Fe (II)	3805	2.4	4.6	5.3
Fe (III)	2246	2.9	5.6	7.7
Ni (II)	5373	2.2	5.0	6.9
Zn (II)	33334	5.9	8.0	9.8

Table: 6.4: The calculation of the equilibrium formation constants of the studied metal ions have also been worked out with respect to complexation with acetate

Metal Ion	D_o	log k_1	log β_2	log β_3
Mg(II)	562866076	9.5	10.4	10.6
Mn(II)	7232	8.1	8.7	9.6
Fe(II)	66510752	4.3	5.1	5.4
Fe(III)	46367786	7.1	8.3	8.6
Ni(II)	37762816	7.9	8.4	9.3
Zn(II)	2198016	7.8	8.9	9.3
Al(III)	10403231	6.5	7.4	7.6

The formation constant values were compared with the reported literature(19) values and it has been observed that these are neither so close nor so different and deviations are associated with the mixed ligand effects. It has also been found in case of certain investigated metal ions, the formation constant values are high to literature values, similar observations found in cases of acetate systems were the literature values are very less.

Table-6.5: Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal Ion	Experimental value λ_3	Calculated value λ_3	λ_2	β_3	β_2	Experimental value $\lambda_3\beta_3$	Calculated value $\lambda_3\beta_3$	$\lambda_2\beta_2$
Mg(II)	240	259	1093	6516606	4563	527332080	1563985494	4989669
Mn(II)	328	336	601	575947	5378	116956272	188910778	3234093
Fe(II)	18.1	17.3	36	2724876	16645	49320256	45090020	607498
Fe(III)	100	101	64	1114250	3527	139914800	111425033	225806
Ni(II)	116	142	58	517470	15152	59923026	32710628	884642
Zn(II)	87.5	83.4	1100	2274498	662	192256488	199018587	728243
Al(III)	66.6	214	83	243000	2627	198564970	16183819	218241

Table-6.6: Log Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal ion	Experimental λ_3 value	Calculated λ_3 value	$\log\lambda_3$	$\log\beta_3$	$\log\beta_2$	$\log\lambda_2\beta_2$	$\log\lambda_3\beta_3$
Ni(II)	2.38	2.41	2.1	5.7	4.2	5.9	7.8
Zn(II)	2.52	2.53	1.9	6.4	2.8	5.9	8.3
Mg(II)	1.26	1.24	2.4	6.8	3.7	6.7	9.2
Mn(II)	2.00	2.00	2.5	5.8	3.7	6.5	8.3
Fe(II)	2.06	2.15	1.3	6.4	4.2	5.8	7.7
Fe(III)	1.94	1.92	2.0	6.1	3.5	4.9	8.1
Al(III)	1.82	2.33	1.8	5.4	3.4	5.3	7.2

Systematic ion exchange characterization of Mg(II), Mn(II), Fe(II and III), Ca(II), Ni(II), Co(II), Cu(II), Zn(II) and Cd(II) ions in aqueous ammonium citrate media have been studied and results were reported as the distribution behaviours and the D-values of the metal ions in the concentration range between 1.00×10^{-3} M to 7.00×10^{-3} M have been reported. Both the anion and cation exchange procedure using Amberlite IR-120 and Amberlite IRA-400 were used to evaluate the equilibrium constant of the investigated metal ions.

Table- 6.7: Values of Distribution Coefficient (D) of (NH₄)₃Cit(OH) media of Amberlite IR - 120 (NH₄⁺ - form)

Concent ration of [Cit] x10 ³	Distribution Coefficient of Metal Ion[3x10 ³]									
	Mg(II)	Mn(II)	Cu(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Co(II)	Ca(II)	Cd(II)
1.00	275.0	400.0	900.0	328.6	400.0	900.0	287.5	500.0	400.0	900.0
1.25	223.9	355.5	733.3	250.6	300.0	700.0	224.2	450.0	326.5	600.0
1.50	172.7	300.0	566.6	172.7	200.0	500.0	160.9	400.0	252.9	300.0
1.75	143.5	244.5	483.3	136.4	157.1	414.3	145.8	364.3	212.8	225.0
2.00	114.3	233.3	400.0	100.0	114.3	328.6	130.8	328.6	172.7	150.0
2.25	107.1	189.5	350.0	93.8	90.5	264.3	112.2	301.8	147.5	121.8
2.50	100.0	172.7	300.0	87.5	66.7	200.0	93.5	275.0	122.2	93.5
2.75	93.8	146.5	268.5	82.0	45.8	165.4	71.8	254.2	104.9	75.7
3.00	87.5	130.8	237.1	76.5	25.0	130.8	50.0	233.3	87.5	57.9
3.25	84.7	114.0	219.3	67.2	21.3	115.4	46.4	203.0	74.8	53.9
3.50	81.8	106.9	201.5	57.9	17.6	100.0	42.9	172.7	62.2	50.0
3.75	79.1	99.8	177.9	50.4	14.4	88.2	39.6	151.7	56.1	46.4
4.00	76.5	87.5	154.2	42.9	11.1	76.5	36.4	130.8	50.0	42.9
4.25	76.5	75.2	135.8	42.9	10.1	67.2	33.4	115.4	50.0	39.6
4.50	76.5	71.4	117.4	42.9	9.1	57.9	30.4	100.0	50.0	36.4
4.75	76.5	67.6	108.4	42.9	7.2	50.4	27.7	88.2	50.0	33.4
5.00	76.5	57.9	99.3	42.9	5.3	42.9	25.0	76.5	50.0	30.4
5.25	76.5	53.5	83.5	42.9	4.4	36.6	22.5	67.2	50.0	27.7
5.50	76.5	50.0	67.6	42.9	3.4	30.4	20.0	57.9	50.0	25.0
5.75	76.5	46.5	55.9	42.9	2.6	25.4	17.7	50.4	50.0	22.5
6.00	76.5	42.9	44.2	42.9	1.7	20.4	15.4	42.9	50.0	20.0
6.25	76.5	39.2	35.3	42.9	1.7	17.9	13.2	38.1	50.0	20.0
6.50	76.5	30.4	26.3	42.9	1.7	15.4	11.1	33.3	50.0	20.0
6.75	76.5	30.4	30.4	42.9	1.7	15.4	9.1	33.3	50.0	20.0
7.00	76.5	30.4	30.4	42.9	1.7	15.4	7.1	33.3	50.0	20.0

Table-6.8: Values of Distribution Coefficient (D) of (NH₄)₃Cit(OH) media of Amberlite IRA - 400 (Cl⁻ - form)

Concentration of [Cit]x10 ³	Distribution Coefficient of Metal Ion[3x10 ³]									
	Mg(II)	Mn(II)	Cu(II)	Fe(II)	Fe(III)	Ni(II)	Zn(II)	Co(II)	Ca(II)	Cd(II)
1.00	36.4	25.0	11.1	30.4	25.0	11.1	36.4	20.0	25.0	11.1
1.25	47.1	29.2	14.4	44.2	37.5	15.6	49.3	22.5	32.3	22.2
1.50	57.9	33.3	17.6	57.9	50.0	20.0	62.2	25.0	39.5	33.3
1.75	72.7	38.1	21.3	71.4	85.0	25.0	69.3	27.7	48.7	50.0
2.00	87.5	42.9	25.0	85.0	120.0	30.0	76.5	30.4	57.9	66.7
2.25	93.8	50.4	29.2	99.6	166.0	40.0	91.7	33.4	69.9	86.8
2.50	100.0	57.9	33.3	114.3	212.0	50.0	106.9	36.4	81.8	106.9
2.75	107.1	67.2	37.8	132.1	306.0	63.2	133.9	39.6	98.0	139.8
3.00	114.3	76.5	42.2	150.0	400.0	76.5	161.0	42.9	114.3	172.7
3.25	118.3	85.0	45.9	161.4	483.3	88.2	197.2	50.4	137.6	186.4
3.50	122.2	93.5	49.6	172.7	566.7	100.0	233.3	57.9	160.9	200.0
3.75	126.5	103.9	57.2	191.4	712.3	115.4	254.2	67.1	180.4	237.5
4.00	130.8	114.3	64.8	210.0	858.0	130.8	275.0	76.4	200.0	275.0
4.25	130.8	127.1	75.0	221.7	1074.5	151.7	301.8	88.2	200.0	301.8
4.50	130.8	140.0	85.2	233.3	1291.0	172.7	328.6	100.0	200.0	328.6
4.75	130.8	156.4	92.9	233.3	1595.5	203.0	364.3	115.4	200.0	364.3
5.00	130.8	172.7	100.6	233.3	1900.0	233.3	400.0	130.8	200.0	400.0
5.25	130.8	186.4	124.3	233.3	2400.0	281.0	450.0	151.7	200.0	450.0
5.50	130.8	200.0	147.9	233.3	2900.0	328.6	500.0	172.7	200.0	500.0
5.75	130.8	216.7	187.0	233.3	4400.0	414.3	575.0	203.0	200.0	500.0
6.00	130.8	233.3	226.1	233.3	5900.0	500.0	650.0	233.3	200.0	500.0
6.25	130.8	280.9	303.0	233.3	5900.0	575.0	775.0	266.7	200.0	500.0
6.50	130.8	328.6	380.0	233.3	5900.0	650.0	900.0	300.0	200.0	500.0
6.75	130.8	328.6	380.0	233.3	5900.0	650.0	1150.0	300.0	200.0	500.0
7.00	130.8	328.6	380.0	233.3	5900.0	650.0	1400.0	300.0	200.0	500.0

The complexation tendencies are effectively determines the metal ion resin interaction where the concentration of the citrate and the exchangeable sorption behaviour of the metal and its charge governed the overall distribution between solution and resin phases. Mg(II) and Zn(II) have shown relatively lowest loading on the cation exchanger at 1.00 x 10⁻³ M citrate indicating the strong complexation while Cu(II), Ni(II) and Cd(II) have also shown the highest sorption at the same citrate concentrations. On increasing the citrate amount the degree of transition metal ion complexation is of the order of Mg(II) or Ca(II), which is not abnormal and is with the agreement of the characteristic of p-and d- block elements but except in

case of Zn(II) all other investigated metal ions have shown a constancy after a particular citrate concentration and from then the d-values become constant. Shubert's approach was used for calculating the formation constant are summarized in the following table

Table 6.9:- Values of formation constant obtained by Shubert's method

Metal Ion	D _o	K ₁	LogK ₁	β ₂	logβ ₂
Mg(II)	5000.0	31923	4.50	-	-
Ca(II)	1056.2	3486	3.54	-	-
Mn(II)	769.2	12545	4.10	635579	5.80
Fe(II)	1191.2	7135.9	3.85	-	-
Fe(III)	1463.2	194630	5.29	212939285	8.33
Ni(II)	2500.0	27409	4.44	41992515	7.62
Co(II)	1428.5	2388.6	3.38	2318071	6.37
Cu(II)	1046.2	594163	5.77	7608051	6.88
Cu(II)	1046.2	594163	5.77	7608051	6.88
Zn(II)	694.3	79025	4.90	19539306	7.29
Cd(II)	6196.2	47324	4.68	8321423	6.92

Likewise the anion exchange experiments have also been performed and the anion exchange sorption tendencies of each metal ion has been determined. All have shown a gradual increase in the citrate concentrations. The nature of sorption pattern is not differing much on comparing one metal by the other. But overall deviations of the individual metal ion has been found closely linked with the complexation factor of the citrate. As well as the anionic nature of the complex species formed and the dissociation of ammonium citrate in the solution. Zn (II) has shown a continuous increase in a sorption with a highest D-value obtained equal to 1400 at 7x 10⁻³M ammonium citrate, while in case of Fe(III) in the same concentration range the value has been obtained equal to 5900. It is also interesting to note that Mg(II) and Ca(II) are p-block elements but their observed behaviour at lower concentration range are closely similar to Ni(II), Fe(II), Mn(II), Co (II), Cu(II), Zn(II), Cd(II) and Fe(III). This confirms the degree of formation of the anionic species for Ca(II) and Mg(II) is of the same order and the nature. It has also been concluded that the affinity criteria of individual metal ion anionic complex species is only slightly higher than the Cl⁻ anion resulting in lower sorption but as the concentration of anionic species formed gradually enhances the nature of anionic species definitely

enhances to more and more sorption at higher concentration ranges of ammonium citrate.

Table 6.10:- Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal Ion	Experimental value λ_2	Calculated value λ_2	λ_1	β_2	β_1	Experimental value $\lambda_2\beta_2$	Calculated value $\lambda_2\beta_2$	$\lambda_1\beta_1$
Mg(II)	-	-	21.6	-	2709	-	-	58517
Ca(II)	-	-	2.26	-	10605	-	-	24015
Fe(II)	-	-	3.5	-	923	-	-	3243
Fe(III)	5900	5899	13354	196639	169	1160170100	1160167518	2261931
Mn(II)	328	328.5	17.6	21486	3339	7059655.02	7059679.9	59089
Ni(II)	650	650.0	-172	259316	165	168555400	168555415	-28344
Zn(II)	1400	1371.1	-5369	1195556	306	1673779408	1639333358	-1643312
Co(II)	300	257.4	10.7	124690	121	37407000	32093662	1304
Cu(II)	380	355.0	136.2	490308	1365	186317317	174069641	186042
Cd(II)	500	488.62	142.6	33618	415	16809000	16426508	59319

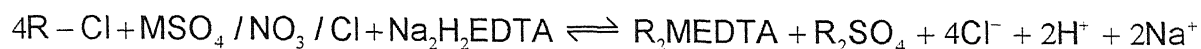
Table 6.11:- Log Values of Distribution coefficients and formation constant obtained by the modified method of Fronaeus

Metal Ion	Experimental value λ_2	Calculated value λ_2	λ_1	β_2	β_1	Experimental value $\lambda_2\beta_2$	Calculated value $\lambda_2\beta_2$	$\lambda_1\beta_1$
Mg(II)	-	-	1.33	-	3.43	-	-	4.77
Ca(II)	-	-	0.35	-	4.03	-	-	4.38
Fe(II)	-	-	0.54	-	2.97	-	-	3.51
Fe(III)	3.77	3.77	4.13	5.29	2.23	9.06	9.06	6.35
Mn(II)	2.52	2.52	1.25	4.33	3.52	6.85	6.85	4.77
Ni(II)	2.81	2.81		5.41	2.22	8.23	8.23	
Zn(II)	3.15	3.14		6.08	2.49	9.22	9.21	
Co(II)	2.48	2.41	1.03	5.10	2.08	7.57	7.51	3.12
Cu(II)	2.58	2.55	2.13	5.69	3.14	8.27	8.24	5.27
Cd(II)	2.70	2.69	2.15	4.53	2.62	7.23	7.22	4.77

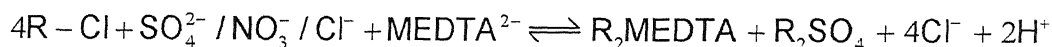
Another new approach was applied to studied ion exchange equilibrium of metal complex species in the resin phase as well as solution phase studies. Ch.-5 is devoted to such a investigations involving the disodium salt of EDTA. Batch equilibration technique was employed for performing the experiment and the resin Amberlite IRA-400 in Cl⁻ form was used. The basic calculated data of the distribution coefficient values of various metal complexes species were evaluated and corresponding ion exchange equilibrium constant were determined, considering the bivalent and trivalent metal-EDTA systems and the corresponding equilibrium equations are proposed. The complexation equilibria for the bivalent and the trivalent metal EDTA-Amberlite IRA-400 systems are given as.

I. Bivalent Metal – EDTA system:-

The complexation and the distribution of the species may be presented by the reactions,



and,



and by the application of law of mass action the ion exchange equilibrium constant (K) may be expressed as,

$$K = \frac{[R_2MEDTA][R_2SO_4][Cl^-]^4[H]^2}{[MEDTA^{2-}][SO_4^{2-}][R - Cl]^4} \text{ or,}$$

$$\lambda = \frac{[R_2MEDTA]}{[MEDTA^{2-}]}$$

$$K = \lambda \frac{[R_2SO_4][Cl^-]^4[H]^2}{[SO_4^{2-}][R - Cl]^4} \text{ or,}$$

Taking log

$$\log K - \log \lambda = \log[R_2SO_4] + 4\log[Cl^-] + 2\log[H^+] - 4\log[R - Cl]$$

Sum of the quantities $\log K - \log \lambda = \log[R_2SO_4] + 4\log[Cl^-] + 2\log[H^+] - 4\log[R - Cl]$

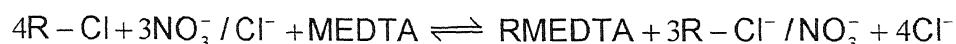
is denoted as Z, then

$$\log K + Z = \log \lambda$$

The plot of Z Vs $\log \lambda$ at zero [L] concentration gives $\log K$ as limiting value of the intercept .

II. Trivalent Metal-EDTA system :-

The complexation and the distribution of the species may be presented by the reaction,



and by the application of law of mass action the ion exchange equilibrium constant (k) may be expressed as,

$$K = \frac{[R_2MEDTA][R - NO_3^-]^3[Cl^-]^4}{[MEDTA][NO_3^-]^3[R - Cl^-]^4} \text{ or,}$$

$$\lambda = \frac{[R_2MEDTA]}{[MEDTA^{2-}]}$$

(λ = Distribution coefficient of complex species, M-EDTA)

$$K = \lambda \frac{[R_2NO_3^-]^3[Cl^-]^4}{[NO_3^-]^3[R - Cl^-]^4} \text{ or,}$$

Taking log

$$\log K - \log \lambda = 3 \log [R - NO_3^-] + 4 \log [Cl^-] - 4 \log [R - Cl^-]$$

$$\text{Sum of the quantities } \log K - \log \lambda = 3 \log [R - NO_3^-] + 4 \log [Cl^-] - 4 \log [R - Cl^-]$$

[is denoted as Z, then

$$\log K + Z = \log \lambda$$

The plot of Z Vs $\log \lambda$ at zero [L] concentration gives $\log K$ as limiting value of the intercept.

On the basis of sorption tendencies of respective anionic metal EDTA complex species it has been observed that the evaluated ion exchange formation constants are decreasing with the increase of metal EDTA concentrations. This behaviour may be correlated with the SO_4^{2-} or the NO_3^- which have stronger sorption in comparison to anionic metal ionic species. But in case of Fe(III) and Ca(II) were instead of SO_4 or the NO_3^- the Cl^- was co-anion therefore, this possibility associated with the exchange of Cl^- can be ruled out as the resin was taken in the Cl^- form. Also the results of Fe(III) and Ca(II) differ from the above mentioned metal ions because they have shown almost constant sorption throughout the investigated range. The

behaviour of La(III)-EDTA species has been found not following trend either of both the metal ion groups described above, instead an increase in the sorption pattern has been observed, which may be contributed by its relatively much high affinity towards the exchanger in comparison to present NO_3^- co-anion. The NO_3^- has also not shown the high sorption related to Cl^- as has been observed in case of Pb(II) and Al(III) which were taken as their NO_3^- solutions.

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